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A simple and precise linear integral method for isoconversional data

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ABSTRACT

A simple and precise linear integral method to evaluate the activation energy dependence on the extent of conversion has been proposed. The method leads to consistent results with those from differential and integral non-linear procedure (Vyazovkin method). Moreover, the new procedure yields the pre-exponential factor and the kinetic model. The method was evaluated from isothermal, non-isothermal and non-linear non-isothermal data (CRTA).

1. Introduction

The wide applicability of the multiple heating-rate methods that are based on several experiments has been proved in the past few years [1–9]. The uncertainty in the calculated value of the activation energy is significantly reduced by using the most common representatives of the multiple heating-rate methods, the isoconversional methods. The merit of such procedures is that the kinetic law (i.e. the mathematical explicit form of the $f(\alpha)$ function, see Table 1) can be ignored completely. Moreover, the isoconversional methods, based on the fact that the reaction rate is only a function of the temperature for a fixed value of α, allow evaluating the dependence of the activation energy on the degree of conversion. Another important success of the isoconversional methods is that when competitive and independent reaction proceed concurrently in a system, the mechanism of the reaction may be revealed by either increasing or decreasing the heating rate [10].

Budrugeac and Segal [11] have criticized the isoconversional method and they state that when the activation energy depends on the degree of conversion, its value obtained by isoconversional differential and integral methods are different, and that the integral isoconversional method produces a systematic error in the activation energy. Vyazovkin [12] has developed an advanced and rigorous non-linear procedure for data obtained under any arbitrary heating program. The differential isoconversional method of Friedman [13] presents the most straightforward way to evaluate the activation energy as a function of the extent of the reaction. The Friedman method make no mathematical approximations, for this reason the systematic error in the activation energy for the linear integral isoconversional method derived assuming a constant activation energy does not appear in the differential method of Friedman. For this reason one can estimate the systematic error of an integral isoconversional method by comparing it against the Friedman method. But this method employs instantaneous rate values and it is very sensitive to experimental noise, although the advent of software with smoothing capabilities has greatly reduced this disadvantage. This situation is effectively avoided by using the isoconversional method in its integral form. These methods are based on a simplified approximation of the temperature integral. Some approximations of the temperature integral leading to a linear correlation have been developed in order to easily obtain the activation energy, but there are many inaccuracies associated with approximations of the temperature integral. In this paper a simple, but precise, linear integral procedure is proposed without associated inaccuracies.

2. Theoretical

The reaction rate of a heterogeneous reaction is described by the following equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \qquad (1)$$

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Table 1
Set of reaction models to describe the reaction kinetics in solid-state reactions

Symbol	Model	Differential $f(\alpha)$ function	Integral $g(\alpha)$ function
JMA (A_n)	Nucleation and Growth ($n = 0.5$, 1, 1.5, 2, 2.5, 3, 4)	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$	$[-\ln(1-\alpha)]^{1/n}$
F1	First-order	$(1-\alpha)$	$-\ln(1-\alpha)$
R_n	Phase-boundary controlled reaction $n = 0$, 1/2 and 2/3	$(1-\alpha)^n$	$(1-(1-\alpha)^{1-n})/1-n$
D1	1D-diffusion	$1/2\alpha$	α^2
D2	2D-diffusion	$-1/\ln(1-\alpha)$	$\alpha+(1-\alpha)\ln(1-\alpha)$
D3	3D-diffusion (Jander equation)	$[3(1-\alpha)^{2/3}]/[2[1-(1-\alpha)^{1/3}]]$	$[1-(1-\alpha)^{1/3}]^2$
D4	3D-diffusion (Ginstling-Brounshteinn equation)	$3/2[(1-\alpha)^{-1/3}-1]$	$1-2\alpha/3-(1-\alpha)^{2/3}$

the parameters, in this equation, have the usual significance. The reaction models, $f(\alpha)$, most frequently used in solid-state reaction are included in Table 1. It is well known that in several heterogeneous reactions there is a dependence of the effective activation energy on the extent of the reaction [7,14,15]. Thus, when the isoconversional method is used, at a constant extent of conversion α, from Eq. (1) one arrives at:

$$\ln\left(\frac{d\alpha}{dt}\right)_\alpha = \text{const.} - \frac{E_\alpha}{RT} \tag{2}$$

where $\ln(Af(\alpha)) = \text{const.}$

This equation represents the differential isoconversional procedure, and was developed by Friedman [13]. Integration of Eq. (1) leads for a linear heating rate, $\beta = dT/dt$, to:

$$g(\alpha) = A\int_0^t \exp\left(\frac{-E}{RT(t)}\right) dt \tag{3}$$

the integral form of Eq. (3) is represented as:

$$g(\alpha) = \frac{AE}{\beta R} p(x) \tag{4}$$

$p(x)$ is the temperature integral and is given by:

$$p(x) = \int_x^\infty \frac{\exp(-x)}{x^2} dx \tag{5}$$

where $x = E/RT$. This function does not have an exact analytical solution and a large number of approximate equations have been proposed in the literature for performing the kinetic analysis of solid-state reactions. The most popular are those of Coats and Redfern [16], Doyle [17] and Senum and Yang [18], the last of which even at $x = 5$ gives only 0.02% deviation from the exact value of the temperature integral and such deviations do not practically affect the values of the activation energy.

The most popular isoconversional methods are the methods labeled FWO [19,20] and KAS [21,22]. The Flynn–Wall and Ozawa (FWO) integral isoconversional method is based on the Doyle [17] approximation (Eq. (6)) and is one of the method more extensively used as indicated by more than 435 citations received in the last 5 years

$$\ln(p(x)) = -5.331 - 1.052x \tag{6}$$

From Eqs. (4) and (6) one obtains, from a series of non-isothermal curves, $i = 1, \ldots, n$, for a given conversion:

$$\ln\beta_i = \text{constant} - 1.052\frac{\text{Ea}_\alpha}{RT_{\alpha,i}} \tag{7}$$

(Ea stands for approximated activation energy).

Eq. (7) was derived by assuming a constant activation energy. The FWO isoconversional method gives the activation energy from a plot of $\ln\beta$ vs. $1/T$. The Kissinger–Akahira–Sunose (KAS) method was derived using the following $p(x)$ approximation

$$p(x) = \frac{\exp(-x)}{x^2} \tag{8}$$

This expression also leads to a linear isoconversional procedure, thus, from a series of non-isothermal curves ($i = 1, \ldots, n$), for a given conversion, one obtains:

$$\ln\left(\frac{\beta_i}{{T_{\alpha,i}}^2}\right) = \text{constant} - \frac{\text{Ea}_\alpha}{RT_{\alpha,i}} \tag{9}$$

The activation energy is obtained from the plots of the l.h.s of Eq. (9) vs. the reciprocal of the temperature. The FWO and KAS methods use the integrated form of the rate equation assuming constant activation energy and consequently an associated error is unavoidable. The magnitude of this error should be dependent on the magnitude of the variation of E with α and on the value of $x = E/RT$. The relative error $|\delta E/E|(\%)$ of the activation energy calculated by FWO method can be defined by the following expression if we assumed that E and A are constant:

$$\frac{\delta E}{E}(\%) = \left(\frac{\text{Ea}}{E} - 1\right)100 \tag{10}$$

By differentiating Eq. (7) we obtain:

$$\frac{\partial\ln\beta}{\partial(1/T)} = -1.052\frac{\text{Ea}_\alpha}{R} \tag{11}$$

On the other hand from Eq. (4) taking logarithm on obtain:

$$\ln g(\alpha) = \ln\left(\frac{AE}{\beta R}\right) + \ln p(x) \tag{12}$$

for a series of non-isothermal curves recorded at several heating rates, we obtain from Eq. (12) at a constant conversion:

$$\ln\beta = \ln p(x) + \text{constant} \tag{13}$$

When the $p(x)$ function in Eq. (13) is calculated exactly by numerical integration this equation gives the true activation energy E. Therefore, by differentiating Eq. (13) we obtain:

$$\frac{\partial\ln\beta}{\partial(1/T)} = \frac{\partial\ln p(x)}{\partial(1/T)} \tag{14}$$

Since $x = E/RT$ we deduce that:

$$\frac{\partial\ln\beta}{\partial(1/T)} = \frac{E_\alpha}{R}\frac{\partial\ln p(x)}{\partial x} \tag{15}$$

From Eqs. (11) and (15) we deduce that:

$$\frac{Ea_\alpha}{E_\alpha} = \frac{-1}{1.052}\frac{\partial\ln p(x)}{\partial x} \tag{16}$$

From Eq. (10) and (16) it is easy to verify that the relative error of the FWO method can be represented in the form:

$$\frac{\delta E}{E}(\%) = \left(\frac{-1}{1.052}\frac{\partial\ln p(x)}{\partial x} - 1\right)100 \tag{17}$$

Eq. (17) allows calculating the relative error in the activation energy for a given conversion α, and we deduce from this equation that the relative error depend on x and, therefore, on the value of the activation energy.

For the KAS method the relative error was calculated following the same procedure as above, thus by differentiating Eq. (9) we obtain:

$$\frac{\partial \ln \beta}{\partial (1/T)} = -\frac{Ea_\alpha}{R} - 2T \tag{18}$$

From Eqs. (14) and (18) we deduced that:

$$\frac{Ea_\alpha}{E} = -\frac{\partial \ln(p(x))}{\partial x} - \frac{2}{x} \tag{19}$$

and from Eqs. (10) and (19) the relative error in the activation energy is given by:

$$\frac{\delta E}{E}(\%) = \left(-\frac{\partial \ln(p(x)}{\partial x} - \frac{2}{x} - 1\right) 100 \tag{20}$$

we can see from Eq. (20) that the relative error also depend on x and, therefore, on the value of the activation energy. The error decrease with x and increase with the degree of conversion. We can see that the FWO and the KAS methods, which have been derived assuming a constant activation energy, are very sensitive to the $x = E/RT$ values. Thus, for $x = 10$ the deviation in the activation energy for the FWO method is higher than 13% and for $x = 20$ the deviation decreases to 5%. For this reason Vyazovkin [12] has developed an advanced non-linear procedure which uses integration over small time segments as follows, as a result the constancy of E is assumed for only a small segment $\Delta\alpha$:

$$J[E_\alpha, T(t_\alpha)] = \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left(\frac{-E_\alpha}{RT(t)}\right) \mathrm{d}t \tag{21}$$

According to this procedure, for a set of n experiments carried out at different heating program, $T_i(t)$, the value of E_α is determined as the value that minimizes the function:

$$\sum\nolimits_{i=1}^{n} \sum\nolimits_{j\neq i}^{n} \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \tag{22}$$

The associated error is eliminated in this advanced procedure.

2.1. Average linear integral method

When E depend on the degree of conversion the simplified integral methods that use integration from 0 to current α are not appropriate. The average linear procedure proposed here makes use of integration over small intervals of α and thus avoids its limitations. Like the advanced isoconversional methods it makes use of the control over integration by integrating the rate equation over small ranges. Thus for small segment $\Delta\alpha$ the temperature integral can be approximated using the “average or mean value” theorem:

$$J[E_\alpha, T(t_\alpha)] = \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left(\frac{-E_\alpha}{RT(t_\alpha)}\right) \mathrm{d}t \approx \Delta t \exp\left(-\frac{E_\alpha}{RT(t_\alpha)}\right) \tag{23}$$

For small segments $(\alpha - \Delta\alpha, \alpha)$ E and A may be assumed constant, and from Eq. (3) one obtains:

$$g(\alpha - \Delta\alpha, \alpha) = A_\alpha \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left(\frac{-E_\alpha}{RT(t)}\right) \mathrm{d}t \tag{24}$$

From Eqs. (23) and (24):

$$g(\alpha - \Delta\alpha, \alpha) \approx A\Delta t \exp\left(-\frac{E_\alpha}{RT(t)}\right) \tag{25}$$

For a set of n experiments carried out at different heating programs the activation energy can be determined from the logarithmic form of Eq. (25). The “average or mean value theorem” was used before for Popescu [23] to develop an integral method based on the use of degree of conversion measured at the same temperatures on curves recorded at various heating rates. The Popescu’s method is not an isoconversional procedure because it uses, on each curve, a pair of values of conversion at the same temperature, not the same value of conversion at different temperature values. Unlike the Popescu’s method the Average Method is capable of revealing the dependence of the activation energy on the degree of conversion, because most solid-state reactions are not one-step reaction, analysis by the Average Method (like the advanced isoconversional procedure [12]) may reveal this complexity detected as a variation of E with α. Moreover, this new method is based on integration with respect to time that expands the application area to arbitrary heating programs.

2.1.1. Estimation of the pre-exponential factor A and the reaction model g(α)

A simple method is suggested for the estimation of A, the method relies on the application of the compensation effect ($\ln A_\alpha = mE_\alpha + n$). Eqs. (25) allows ones to arrive at Eq. (26)

$$-\ln \Delta t = -\ln \Delta g(\alpha) + mE + n - \frac{E_\alpha}{RT(t)} \tag{26}$$

If we assume the original assumption that the reaction model remains unchanged, $\Delta g(\alpha)$ will be the same and, from the intercept (I) of the linear relationship (26) we obtain:

$$\ln \Delta g(\alpha) + I_\alpha = mE_\alpha + n \quad \text{(where } I \text{ stand for intercept)} \tag{27}$$

Therefore, the compensation parameters m and n may be calculated by fitting the Eq. (27) to the experimental data. Values of m and n have been computed using linear regression, with a choice of the kinetic model of Table 1 that yields the best linear correlation in Eq. (27). From m and n values we obtain the pre-exponential factors. This procedure, based on the intercepts, can not be used with the others linear isoconversional integral methods, FWO and KAS, because of the imprecision of the linear representation and the relative error in the activation energy (Eqs. (17) and (20)). Now we check this procedure with different heating programs.

2.1.2. Linear heating program experiments

For a linear heating program experiments, we can write:

$$\ln g(\alpha - \Delta\alpha, \alpha) \approx \ln \frac{A}{\beta} + \ln \Delta T - \frac{E_\alpha}{RT(t)} \tag{28}$$

With $\beta = \Delta T/\Delta t$.

Thus for a given conversion and a set of experiments performed under different linear heating rates β_i ($i = 1, \ldots., n$):

$$\ln\left(\frac{\beta_i}{\Delta T_{\alpha,i}}\right) = \text{constant} - \frac{E_\alpha}{RT_{\alpha,i}} \tag{29}$$

The activation energy, for each α value, is obtained from the plot of the l.h.s of Eq. (29) vs. the reciprocal of the temperature. The method is very simple and leads to consistent results with those from differential or non-linear isoconversional technique (Vyazovkin method). The precision depends on the precise evaluation of $T_{\alpha-\Delta\alpha}$ and T_α (or $t_{\alpha-\Delta\alpha}$ and t_α).

2.1.3. Isothermal experiments

For a set of isothermal data the dependence of the activation energy on the degree of conversion can be calculated from Eq. (25) for $T = \text{constant}$, thus the following relationship is obtained:

$$-\ln \Delta t_{\alpha,i} \approx \text{constant} - \frac{E_\alpha}{RT_{\alpha,i}} \tag{30}$$

2.1.4. Non-linear non-isothermal experiments (CRTA)

The Average Method can be used for other non-linear non-isothermal processes where the time dependence of the temperature is not simple, or not known, such as CRTA, stepwise isothermal analysis (SIA) or high-resolution thermogravimetry (HRTG). In CRTA experiments the reaction temperatures should be controlled in such a way that both the reaction rate and the partial pressure of the gases produced or consumed in the reaction are maintained at any constant previously selected value. Therefore, Eq. (1) can be expressed in the form:

$$C = Af(\alpha)\exp\left(\frac{-E}{RT}\right) \tag{31}$$

where C is the constant reaction rate. It is easy to verify that from Eq. (25) we obtain, for a given conversion and a set of experiments performed under different constant reaction rates C_i ($i = 1, \ldots., n$):

$$\ln(\Delta t) = \text{constant} + \frac{E_\alpha}{RT_{\alpha,i}} \tag{32}$$

where $\Delta t = \Delta\alpha/C$

The dependence of the activation energy on the conversion α is obtained from the plot of the l.h.s of Eq. (32) vs. the reciprocal of the temperature.

2.2. Simulations

It is well known that many solid-state reactions show a dependence of the activation energy on the degree of conversion α. The occurrence of such dependence could be interpreted in terms of a complex reaction mechanism [15]. For example, a variation of the effective activation energy may be observed for a process that involves two parallel first-order reactions with two different activation energies. The overall rate of this process is given as:

$$\frac{d\alpha}{dt} = A1\exp\left(-\frac{E1}{RT}\right)(1-\alpha) + A2\exp\left(-\frac{E2}{RT}\right)(1-\alpha) \tag{33}$$

For four linear heating rates of 1, 2, 4 and 8 °C min^{-1} where $E1 = 167$ kJ mol^{-1}, $A1 = 10^{12}$ min^{-1}, $E2 = 351$ kJ mol^{-1} and $A2 = 10^{26}$ min^{-1}, the values of the activation energies obtained from the Friedman method are shown in Fig. 1. We can see that, in this case, there is a good linear dependence of the effective activation energy on the degree of conversion α:

$$E = 169.4 + 95.3\alpha \tag{34}$$

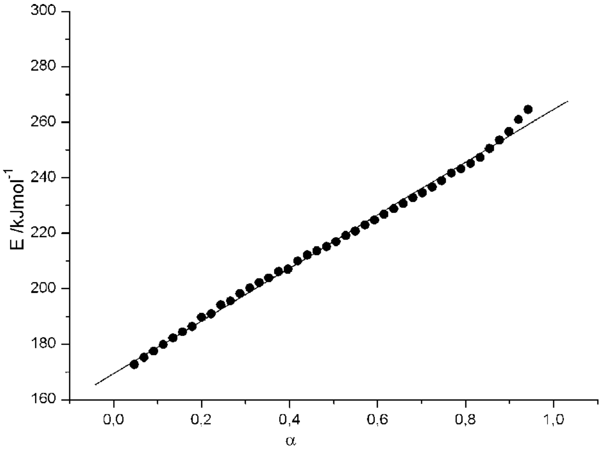

Fig. 1. E_α dependence evaluated for the simulated process (parallel first order reactions) by the Friedman method.

In this paper, we use this result to calculate simulated processes that involves a linear variation of the effective activation energy with α, such as:

$$E_\alpha = Eo + b\alpha \quad (\text{where } b \text{ is a constant}) \tag{35}$$

When E depends on the degree of conversion α, the apparent activation parameters (E and A) are correlated through the compensation effect relationship which is the consequence of the application of the Arrhenius equation. In accordance with this, only one value of A correspond to each E value [14,24–26]. Thus, in this paper the following relationship is used:

$$\ln A_\alpha = mE_\alpha + n = m(Eo + b\alpha) + n \tag{36}$$

Different heating programs have been simulated: linear non-isothermal, isothermal and non-isothermal non-linear experiments such as controlled rate thermal analysis (CRTA). All the data were simulated for first order reactions, F1, i.e., $f(\alpha) = 1 - \alpha$. The following kinetic parameters have been used:

- For isothermal experiments: $Eo = 100$ kJ mol^{-1}; $b = 30$ in Eq. (35). and $m = 0.2$, $n = -1.0$ in Eq. (36) and the following isothermal temperatures: 550, 560, 570 and 580 K
- For non-isothermal experiments: $Eo = 50$ kJ mol^{-1}; $b = 30$ and $m = 0.1$, $n = -1.0$ and the following heating rates: 1, 2, 3 and 4 K min^{-1}
- For non-linear non-isothermal experiments (CRTA): $Eo = 100$ kJ mol^{-1}; $b = 30$ and $m = 0.2$, $n = -1.0$ and the following constant reaction rate C: 3×10^{-5}; 6×10^{-5}; 9×10^{-5}; 1.2×10^{-4} min^{-1};

Fig. 2 shows the dependence of the activation energy evaluated by means of different isoconversional methods for isothermal data (Eq. (30)).

Fig. 3 shows the dependence of the activation energy on the degree of conversion evaluated for the non-isothermal data (linear heating rate (Eq. (29))).

Finally Fig. 4 shows the dependence of the activation energy for the non-linear non-isothermal experiment, CRTA data (Eq. (32)).

2.2.1. Evaluating the pre-exponential factor and the kinetic model

Isoconversional methods identify the dependence of E on α but do not yield the pre-exponential factor and the reaction model but with the Average Method here proposed the estimation of the pre-exponential factor and the kinetic model have been carried out

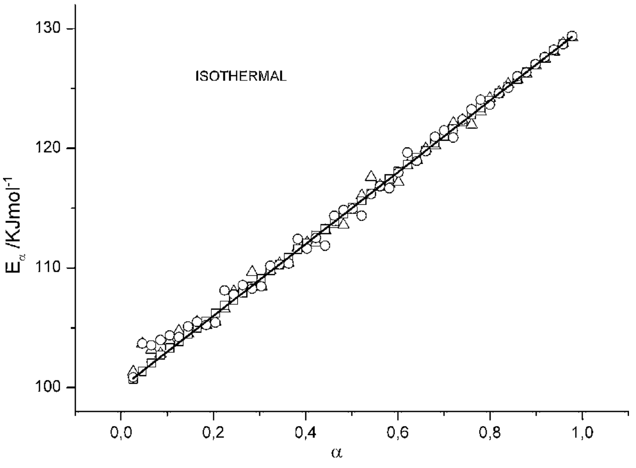

Fig. 2. Dependence of E on α, for isothermal data, evaluated by means of the Average Method (○), Advanced Vyazovkin (△) method and the Friedmann (□) method. The solid line represents the E simulated value from Eq. (35).

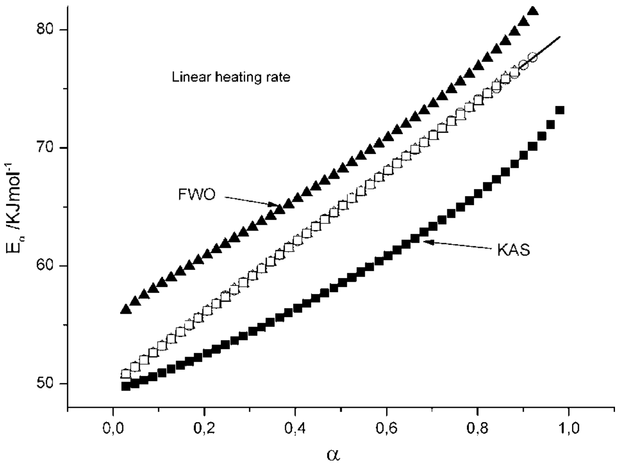

Fig. 3. Dependence of E on α for non-isothermal data evaluated by different isoconversional procedures: the Average Method (○), the Advanced Vyazovkin (△) method, the Friedmann (□) method (the three are superposed) and the KAS and FWO methods. The solid line represents the E simulated values from Eq. (35).

using the method proposed above (Eq. (27)). This procedure has been checking using the simulated non-isothermal data with $\beta = 1$, 2, 3 and 4 K min^{-1} (similar results have been obtained from isothermal and CRTA data, these results have not been included for the sake ob brevity). Fig. 5 shows a plot of Eq. (27) for all the reaction models, and we can see that, of the reaction models of Table 1,the first-order reaction model, F1, provide the best linearity, this agree with the kinetic model assumed for the calculation.

Fitting of the reaction model followed by linear regression analysis resulted in the following compensation parameters: $m = 0.101$ and $n = -0.998$ this agree well with the initial assumptions ($m = 0.1$ and $n = -1$). As a result, the pre-exponential factor A can be calculated from the relationship ($\ln A_\alpha = mE_\alpha + n$), these results are included in Fig. 6.

Finally, the new procedure has been checked for a set of parallel first-order consecutive reactions and the following kinetic parameters: $E1 = 84\,\text{kJ mol}^{-1}$; $A1 = 6 \times 10^6\,\text{min}^{-1}$; $E2 = 335\,\text{kJ mol}^{-1}$; $A2 = 1.8 \times 10^{29}\,\text{min}^{-1}$ and the heating rates: 1, 2, 3 and 4 K min^{-1}. The system of differential equations is given by Eq. (33). The simulated data have been processed by the differential method of Friedmann and by integral isoconversional methods. The FWO and KAS methods give rise to a dependence of E on α which

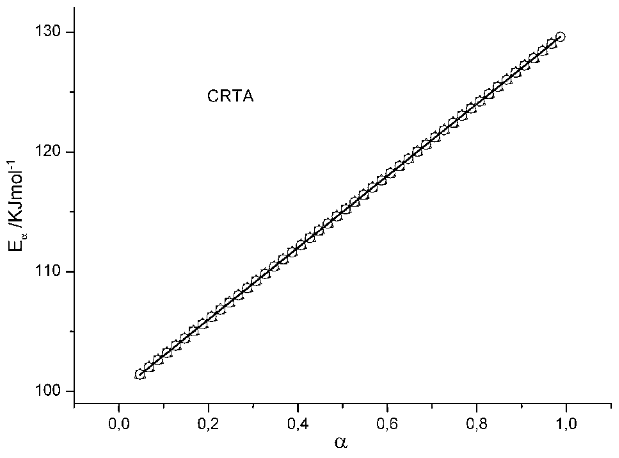

Fig. 4. Dependence of E on α, for CRTA data, evaluated by means of the Average Method (○), Advanced Vyazovkin (△) method and the Friedmann(□) method (the three methods are superposed). The solid line represents the E simulated value from Eq. (35).

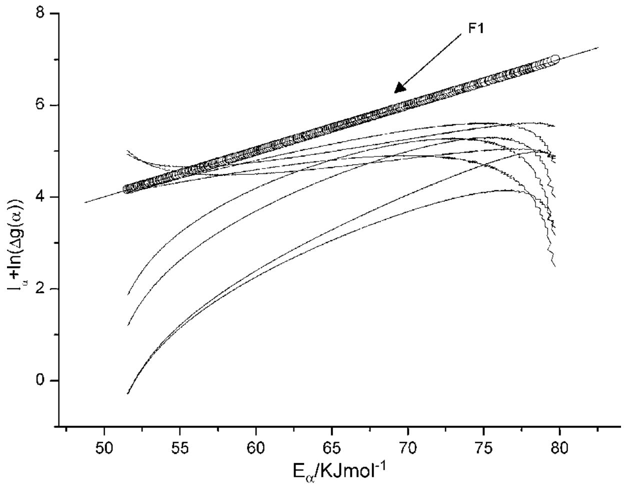

Fig. 5. Evaluation of the kinetic model from Eq. (27) (values of $I_\alpha + \ln \Delta g(\alpha)$ against E_α for all the kinetic models of Table 1).

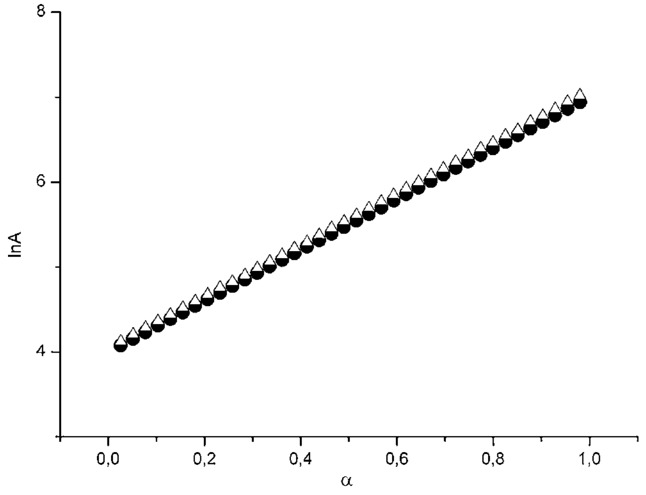

Fig. 6. Dependence of $\ln A$ on α for non-isothermal data evaluated by means of the Average Method (△) ($\ln A_\alpha = mE_\alpha + n$), solid circles indicate the simulated data assumed for the calculation of the theoretical curves.

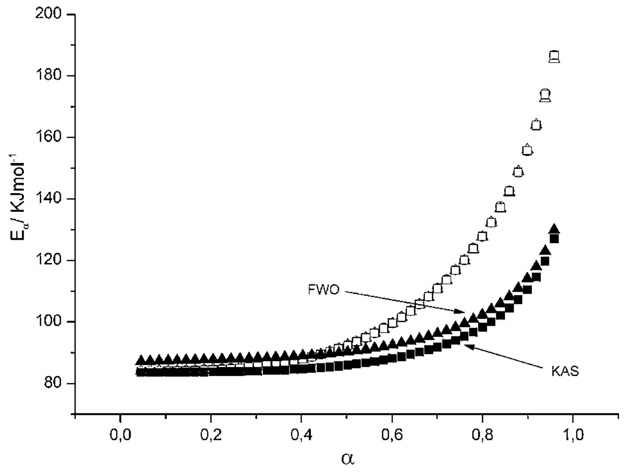

Fig. 7. Dependence of E on α evaluated by means of isoconversional methods for two parallel first-order consecutive reactions. The Average Method (○) the Advanced Vyazovkin) method (△) and the Friedmann (□) method are superposed.

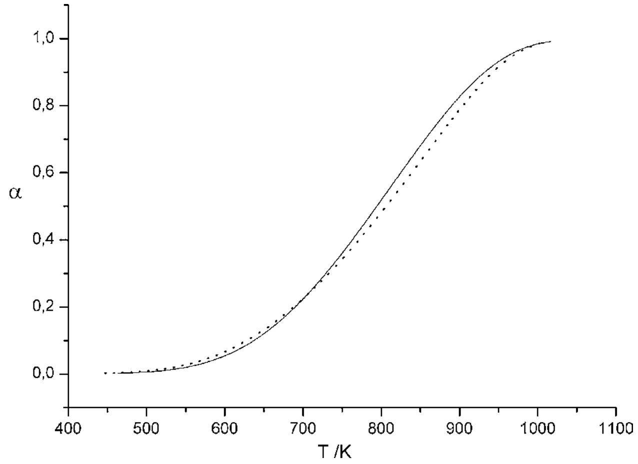

Fig. 8. Comparison of the simulated non-isothermal TG curve at a heating rate of $\beta = 2$, solid line, with the corresponding TG curve generated using the kinetic triplets calculated from the Average Method (dotted line).

deviates from the dependence estimated by the others methods. The Average Method yields a dependence which is practically identical to that estimated by the differential and the Vyazovkin methods. These dependences are shown in Fig. 7.

2.2.2. *Kinetic predictions*

It has been shown that the isoconversional method reveals the dependence of E on the degree of conversion, this dependence is a source of kinetic information and helps, not only to disclose the complexity of the process, but also to identify its kinetic model as well.

Knowing values of the kinetic triplet one can predict a dependence of α on T. To make kinetic predictions it is necessary to generate data from the kinetic triplet determined here. The kinetic parameters obtained from non-isothermal data using the Average Method have been used to generate data for comparison with initial simulated data. From the values of the kinetic triplets (E, A and $g(\alpha)$) obtained from the Average Method we generate in Fig. 8 a thermoanalytical curve at a heating-rates of 2 K min^{-1}. Similar results have been obtained for the others heating rates.

3. Conclusions

An integral isoconversional procedure have been deduced from the "average or mean value" theorem to evaluate the activation energy from isothermal, linear non-isothermal and non-linear non-isothermal data (CRTA). When the activation energy changes with the conversion α the Average Method here proposed leads to E values identical with those obtained by Friedmann and by the advanced non-linear procedure of Vyazovkin [12]. Moreover, this procedure, on the contrary that the others linear isoconversional method, yields the pre-exponential factor and the kinetic model (with the assumption that the function $g(\alpha)$ remains the same when changing temperature). The new procedure is very simple and precise.

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