Integral, differential and advanced isoconversional methods
Complex mechanisms and isothermal predicted conversion–time curves

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A B S T R A C T
Differences in the activation energy values determined from differential and integral isoconversional methods have been already reported. For a long time it was believed that these differences could be due to the approximations used for the temperature integral used in integral methods. In fact, this study clearly shows that the assumption of a constant activation energy is a key parameter that must be considered in the case of a complex reaction mechanism leading to a great variation of the effective activation energy on conversion. The study also shows that the advanced integral method of Vyazovkin gives more accurate results. For short time predictions, all the methods tested gave satisfactory results but for long time simulations the conventional integral methods may lead to inaccurate outcomes.

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1. Introduction

   Isoconversional methods have been known for many years [1–6]. These methods yield the values of effective activation energy as a function of conversion. Nevertheless, except the pioneering work of Flynn and Wall [5], the obtained variation of the activation energy on conversion was more considered as a problem than as a powerful source of information that could be used for elucidation of the kinetic mechanism of the overall process under study.

   More recently, some papers have shown how a complete isoconversional kinetic analysis can be performed using the dependence of the activation energy on conversion, in association with various thermo-analytical data like dynamical scanning calorimetry (DSC), rheometry, dynamical mechanical analysis (DMA) and thermogravimetry (TGA) [7–9]. Model-free isoconversional methods are among the most reliable for determining activation energies of thermally stimulated complex processes. Recently, these methods have been widely used to study the kinetics of chemical or physical processes and allow to draw important conclusions on the mechanisms of various chemical reactions, cross-linking, renewable thermosets, polymer crystallization, glass transition kinetics, thermal and thermo-oxidative degradation, protein denaturation and glass aging [8–22].

   Simulations are also very important for industrial purposes. For example, isothermal simulations derived from nonisothermal data allow the computation of the complete conversion–time curves at a given temperature (called isothermal "predictions"). Isoconversional methods can be used for optimization and safety purposes because all the simulations performed with usual kinetic parameters (obtained from traditional methods) can be realized using the sole activation energy dependency. An important aspect for industry is that these simulations may be done in a model-free way, i.e. without any assumption on the reaction mechanism (model-free kinetics).

   For non-isothermal data, isoconversional methods require performing a series of experiments at different temperature programs. The most popular methods are represented by the differential method of Friedman (FR) [1] and by the integral methods proposed by Ozawa–Flynn–Wall (OFW) [2,5] or Kissinger–Akahira–Sunose (KAS) [3,4]. These methods will be referred as conventional isoconversional methods. More recently, Vyazovkin has proposed an advanced non-linear method (NLN) [23,24].

   Integral isoconversional methods, such as OFW and KAS, are limited to the use of a linear variation of the temperature and positive heating rate. Thus, these latest methods are not applicable to cooling (as for the study of crystallization kinetics from the melt) [15]. The advantage of the differential FR method is that it is free of approximations and is not limited to the use of a linear variation of the heating (or cooling) rate. However, it has been shown that the method proposed by Friedman may lead to systematic errors when the reaction heat significantly changes with the heating rate [25].

   Differences in the activation energy values determined from differential and integral isoconversional methods have frequently been reported [14,26]. For a long time, it was believed that the approximation used for the temperature integral (integral methods) was at the origin of this phenomenon. For this reason, many authors have compared the accuracy of these methods using simulated and experimental data [26–32]. Numerous works have been done to
estimate the error introduced by using various approximations for the temperature integral, called \( p(x) \) [31–33]. Indeed, in the case of a single step process, it was shown that the OFW method (integral) can give similar results with the FR method (differential), if a numerical procedure is used to compute \( p(x) \) [26]. Nevertheless, in the case of a strong dependence of activation energy on conversion, as is the case of many complex processes, this correction has little effect, and differential and integral methods lead to different \( E_a \)-dependencies [26]. This statement was confirmed later [29]. In this study, we present a comparison between isoconversional methods of Friedman (FR), Ozawa–Flynn–Wall (OFW), Kissinger–Akahira–Sunose (KAS), the advanced non-linear method of Vyazovkin (NLN) and the Ozawa method corrected by evaluating the temperature integral numerically (OFWC) as proposed by Shirrazzuoli et al. [26]. The comparison between FR and NLN, gives new insights and permits to explain the origin of the differences observed between differential and integral methods.

This comparison was performed using simulated differential scanning calorimetry (DSC) data and an experimental example of epoxy cure [12]. Nevertheless, the obtained conclusions could be applied to other thermoanalytical techniques. The accuracy of each method is presented for the case of a single-step process, with and without additional artificial noise, as well as for the case of a complex mechanism. Additional noise was used in order to simulate conditions closer to real experimental data and to check the robustness of each method vs. random errors. The effect of the errors in the activation energy values on the accuracy of short and long term isothermal predictions is also presented.

2. Theoretical approaches

2.1. Isoconversional method by differential equations

The overall rate of reactions is commonly described by the equation

\[
\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}
\]

where \( \frac{d\alpha}{dt} \) is the reaction rate, \( \alpha \) is the conversion degree, \( k(T) \) is the rate constant, \( t \) is the time, \( T \) is the temperature, and \( f(\alpha) \) is the reaction model. The dependence of the rate constant is traditionally described by the Arrhenius law

\[
k(T) = A \exp \left( -\frac{E}{RT} \right) \tag{2}
\]

where \( E \) is the activation energy, \( A \) is the preexponential factor and \( R \) is the gas constant.

Using Eqs. (1) and (2), the expression proposed by Friedman [1], that allows to determine the activation energy \( E \) for each given conversion degree, can be presented as:

\[
\ln \left( \frac{d\alpha}{dt} \right)_{\alpha,i} = \ln \left[ A_{a,i} f(\alpha) \right] - \frac{E_a}{RT_{\alpha,i}} \tag{3}
\]

where the subscript \( i \) denotes the ordinal number of a non-isothermal experiment conducted at the heating (or cooling) rate \( \beta_i \) and the subscript \( \alpha \) the quantities evaluated at a specific conversion degree \( \alpha \). The heat flow measured in DSC is proportional to the overall heat release and to the rate of the transformation. In DSC, the conversion degree \( \alpha \) is defined as the ratio between the heat exchanged at time \( t_i \) \((\Delta H)\) and the total heat released by the reaction \((Q)\). Accordingly, Eq. (3) can be rewritten as

\[
\ln \left( \frac{d\alpha}{dt} \right)_{\alpha,i} = \ln \left[ QA_{\alpha,i} f(\alpha) \right] - \frac{E_a}{RT_{\alpha,i}}. \tag{4}
\]

Evaluation of the activation energy from the plot of the left side of Eq. (4) vs. \( 1/T_{\alpha,i} \) at constant conversion degree, for the used \( i \) heating or cooling rate, will be called the Friedman method (FR).

Despite the use of a general form for the reaction model \( f(\alpha) \) in Eq. (1), this equation only holds for a single-step reaction mechanism and implies that the postulated reaction mechanism is the same over the whole temperature range of the nonisothermal experiment. In contrast, the basic idea of isoconversional methods can easily be understood by differentiating Eq. (3) vs. \( 1/T \) that gives

\[
\frac{d\ln(\alpha)}{dT} = -\frac{E_a}{R} \tag{5}
\]

This equation means that the reaction rate is only a function of temperature at a constant conversion degree. In contradiction with Eq. (1), this equation only assumes that the reaction model is the same for a constant value of the conversion degree and not over the whole temperature range of the nonisothermal experiment. Because non-isothermal isoconversional methods require the use of \( i \) scanning rates to compute the activation energy Eq. (4) these methods only assume that the reaction model is the same for all the \( i \) heating rates at a given value of the conversion degree (and not over the overall temperature interval where the reaction occurs).

2.2. Isoconversional methods by integral equations

2.2.1. Kissinger–Akahira–Sunose (KAS) method

Using a linear heating rate \( \beta = dT/ dt \) Eq. (1) can be written:

\[
\frac{d\alpha}{dt} = k(T) f(\alpha) / \beta \tag{6}
\]

and

\[
\frac{d\alpha}{dT} = \frac{A}{\beta} \exp \left( -\frac{E}{RT} \right) f(\alpha) \tag{7}
\]

\[
g(\alpha) = \frac{A}{\beta} \int_0^{\infty} \exp(-E / RT) dT \tag{8}
\]

which does not have an analytical solution. Eq. (8) is sometimes written as [34]:

\[
g(\alpha) = \frac{AE}{R^3} \left[ \exp\left( \frac{-E}{x} \right) - \int_{x}^{\infty} \exp\left( \frac{-E}{x} \right) dx \right] = \frac{AE}{R^3} p(x) \tag{9}
\]

where \( x = E / RT \) is the reduced activation energy at the temperature \( T \). The function \( p(x) \) can be replaced by a number of useful approximations, which have been discussed by Flynn [35]. Note that Eq. (9) assumes a constant value of \( E \).

The Kissinger–Akahira–Sunose method (KAS) [3,4] is obtained using \( p(x) = e^{-x} / x^2 \), which is valid for \( 20 \leq x \leq 50 \):

\[
\ln \left( \frac{\beta_i}{T_{\alpha,i}^2} \right) = \ln \left( \frac{A_{a,i} R}{E_a} \right) - \ln g(\alpha) - \frac{E_a}{RT_{\alpha,i}}. \tag{10}
\]

Evaluation of the activation energy from the plot of the left side of Eq. (10) vs. \( 1/T_{\alpha,i} \) at constant conversion degree for the \( i \) used heating rate \( (\beta_i) \) will be called the Kissinger–Akahira–Sunose method (KAS).

2.2.2. Ozawa–Flynn–Wall method

Using Doyle’s approximation [36]:

\[
\ln(\alpha) = -5.3305 - 1.052x \quad (20 \leq x \leq 60) \tag{11}
\]
the linear equation of Ozawa–Flynn–Wall can be obtained [2,5]:
\[
\ln \frac{\alpha_i}{(1 - \alpha_i)} = \ln \left( \frac{E_{\alpha_i} A_{\alpha_i}}{R} \right) - \ln g(\alpha_i) - 5.3305 - 1.052 \left( \frac{E_{\alpha_i}}{R T_{\alpha_i}} \right)
\] (12)

Evaluation of the activation energy from the plot of the left side of Eq. (12) vs. 1/T_{\alpha_i} at constant conversion degree for the i heating rate used will be called the Ozawa–Flynn–Wall method (OFW).

2.2.3. Ozawa–Flynn–Wall corrected method
We have proposed a different way to obtain corrected activation energy values using a numerical integration of p(x). This method consists in computing E_{\alpha_i} at a given conversion (OFW method). Then, the mean temperature value (T_{\alpha_i}) over the various heating rates is evaluated and the expression of p(x) is estimated by a numerical integration of Eq. (9). Then, in p(x) values are fitted by a first order polynomial on the interval x = E_{\alpha_i} (1 ± 0.2) / (R T_{\alpha_i}), for each given conversion. This method will be refered as the corrected Ozawa–Flynn–Wall method (OFWC) [26]. In 2001, Gao has proposed a correction of the OFW method based on an iterative procedure, after an initial estimate of E_{\alpha_i} using the usual OFW method [37].

In comparison with Friedmann method, integral methods do not use the measured heat flow, but are only valid for a linear positive heating rate (Eqs. (6), (10), (12)).

2.2.4. Non-linear integral isoconversional method
The advanced isoconversional method proposed by Vyazovkin [23] is free of the approximations used in KAS and OFW methods because it is based on a direct numerical integration of Eq. (8). In contrast with other integral isoconversional methods (KAS, OFW and OFWC), it takes into account a possible variation in the activation energy. According to this method, for a set of n experiments carried out at different arbitrary heating programs T_i(t), the activation energy is determined at any particular value of α by finding the value of E_{\alpha_i} that minimizes the function
\[
q_i(E_{\alpha_i}) = \sum_{i=1}^{n} \sum_{j \neq i}^n \left| \frac{E_{\alpha_j} T_i(t_{\alpha_i})}{E_{\alpha_j} T_j(t_{\alpha_j})} \right|
\] (13)

ln Eq. (13), the integral
\[
\int[E_{\alpha_i} T_i(t_{\alpha_i})] = \int_{t_{\alpha_i} - \Delta \alpha}^{t_{\alpha_i}} \exp \left[ -\frac{E_{\alpha_i}}{R T_i(t)} \right] dt
\] (14)

is evaluated numerically, using the trapezoid rule, for a set of experimental heating programs. Integration is performed over small time segments (Eq. (14)) that allows to eliminate the systematic errors occurring in the usual integral methods when E_{\alpha_i} varies significantly with α. In Eq. (14), α is varied from Δα to 1 − Δα with a step Δα = m^{-1}, where m is the number of intervals chosen for analysis [24].

All these kinetic methods were programmed in an in–house software, already described and regularly upgraded [25,26,38]. For all the methods previously described to determine the E_{\alpha}-dependence, the minimization procedure is repeated for each value of α (0.01 < α < 0.99, each 0.01 α value).

3. Simulated example

3.1. Single step mechanism

Let us consider a simple single-step process that follows a reaction order model. The overall rate of this process is given by Eq. (15)
\[
\frac{dx}{dt} = k(T)(1 - \alpha)^{n}
\] (15)

where n is the reaction order and k(T) is the rate constant. These simulations consist in the computation of the temperature (T), the power (P_i) and the conversion degree (α_i) using a procedure already described [39]. The following parameters were used: starting temperature of the simulations T_0 = −20 °C, sampling rate Sr = 1 s, heating rates β = 2, 5 and 10 K min^{-1}, reaction heat Q = 100 J g^{-1}, sample mass m = 20 mg, activation energy E = 80 kJ mol^{-1}, logarithm of the preexponential factor ln(A / s^{-1}) = 19, reaction order n = 1. The computations were stopped when (1 − α) was smaller than 10^{-11}.

3.2. Simulated data with pseudo-Gaussian random noise
In order to compare the robustness to experimental errors of each method, artificial pseudo-Gaussian random noise was generated (mean = 0 and standard deviation σ = 0.05 mW) [40]. The characteristics of the noise were chosen according to the isothermal measurement of a curing reaction [12]. The standard deviation of the baseline of an isothermal measurement at 120 °C obtained when the reaction was achieved was less than 0.05 mW (about 0.03 mW).

3.3. Complex mechanism

A simple case of complex mechanism of two parallel reactions (noted A and B) governed by a reaction order model was simulated. This mechanism can be represented by the following equation:
\[
\frac{dx}{dt} = k_A(T)(1 - \alpha_A)^{n_A} + k_B(T)(1 - \alpha_B)^{n_B}
\] (16)

The parameters used in the simulations were taken as: T_0 = −20 °C, Sr = 1 s, heat of the exothermic effects Q_A = 60 and Q_B = 40 J g^{-1}, kinetic orders n_A = 1, n_B = 1; activation energies E_A = 80 and E_B = 120 kJ mol^{-1}, logarithms of the pre-exponential factor ln(A_A / s^{-1}) = 19, ln(A_B / s^{-1}) = 30, sample mass m = 20 mg [41]. The computations were stopped when (1 − α) was smaller than 10^{-11}. The procedure was used to simulate both isothermal (temperatures of 80 and 110 °C) and non-isothermal (heating rates β = 0.5, 2, 5 and 10 K min^{-1}) data. These values lead to x varying between 29 and 38 (29<x<38).
4. Results and discussion

4.1. Simulated data applied to a single step mechanism

The obtained simulated thermoanalytical curves were already presented [25] and the resulting $E_\alpha$-dependencies are shown in Fig. 1. As shown, all the methods give similar results, excepted OFW. For the FR, KAS, OFWC and NLN methods the $E_\alpha$ values are very close to the simulated value of 80 kJ mol$^{-1}$. For example, the $E_\alpha$ values for $\alpha = 0.50$ are respectively 80.00, 79.77, 82.03, 80.13 kJ mol$^{-1}$ for FR, KAS, OFW and OFWC methods. The value is 80.00 kJ mol$^{-1}$ for NLN method.

More accurate results are given by FR and NLN methods, while the less accurate value is given by OFW method. Because the OFW method leads to more accurate values when a numerical procedure is used for the computation of $p(x)$ (OFWC), it can be confirmed that the lower accuracy of this method can be attributed to the error induced by the use of a less accurate approximation for $p(x)$. These results clearly show that using simulated data, very accurate results can be obtained if the methods are properly programmed and if an appropriate interpolation algorithm is used to compute temperature and heat flow for each $\alpha$ value. For illustration, the mean of each absolute relatives error ($e_{\text{mean}}$) for $\alpha$ for each methods over the interval 0.02–$\alpha=0.98$, are $9.7 \times 10^{-4}$, $32.4 \times 10^{-4}$ (step on $E=10^{-2}$), $2799.0 \times 10^{-4}$, $25031.4 \times 10^{-4}$, $15683.1 \times 10^{-4}$ respectively for FR, NLN, KAS, OFW and OFWC methods (NLN step on $E=10^{-5}$, $e_{\text{mean}} = 8.5 \times 10^{-4}$). Even if this accuracy is unrealistic for experimental data, it is important to ensure first that the algorithms used have such precision otherwise a comparison of the accuracy of each method and of time predicted curves is meaningless.

4.2. Simulated data with pseudo-Gaussian random noise

The obtained simulated thermoanalytical curves are presented in Fig. 2 and the resulting $E_\alpha$-dependencies are shown in Fig. 3a and b. As shown in the inset of Fig. 2, the simulated artificial pseudo-Gaussian random noise used corresponds to a relatively high perturbation of the signal for low and high conversion degrees at the lower heating rates, compared to the actual quality of the signal generated by modern thermoanalytical instruments. This explains the higher errors in the $E_\alpha$ values observed at low and high conversion degrees using all the methods under investigation. Note that KAS, OFW and OFWC are more stable for high values of the conversion degree. Nevertheless, these values must be interpreted with care, because the results of the computations on noisy data are depended to the integration bounds selected. Nevertheless, the accuracy can be easily improved using a simple smoothing algorithm applied to the simulated thermoanalytical curves, as shown in the inset of Fig. 3a and b (an internally generated software Testpoint® was applied to the data). According to these results it can be concluded that these methods give accurate $E_\alpha$ values even in the case of noisy data.

4.3. Simulated data on a complex mechanism

The obtained simulated thermoanalytical curves are presented in Fig. 4. The data presented in Fig. 5 give the $E_\alpha$-dependencies obtained for non-isothermal simulated DSC data in the case of the complex mechanism previously described. As can be seen, FR and NLN methods give a first set of very similar results, while KAS, OFW and OFWC give a second set of similar results, different from those obtained with FR and NLN. The difference between FR and integral methods cannot be attributed to a possible instability of differential method because FR method gives similar results to the NLN method. On the other hand, this difference cannot be attributed to the error for the approximation...
of the temperature integral because this difference still exists between FR and OFWC methods. So, it can be concluded that, in the case of a complex mechanism leading to a great variation of the effective activation energy on conversion, the approximation of a constant activation energy in the computation of the temperature integral is responsible for the differences in the activation energy values determined from differential and integral isoconversional methods.

By combining Eqs. (5) and (16) we obtain:

$$E_\alpha = \frac{0.60E_1k_1(1 - \alpha_1) + 0.40E_2k_2(1 - \alpha_2)}{0.60k_1(1 - \alpha_1) + 0.40k_2(1 - \alpha_2)}$$  \hspace{1cm} (17)

From this equation two interesting limiting cases can be obtained. If $\alpha_1 \to 1$, then $E_\alpha \to E_2$. Furthermore, at the beginning of the reaction $\alpha_1$ and $\alpha_2 \to 0$ (as presented in Fig. 4) and $k_2 \ll k_1$, then $E_\alpha \to E_1$. At the very beginning of the reaction, the complex mechanism tends to a single step reaction involving a single activation energy value. Because at the beginning of the reaction the actual temperature $T$ is close to the temperature of the first integration bound ($T_0 = -20 ^\circ C$), the error due to the approximation of a constant value of $E$ for the temperature integral over $T_0$ and $T$ is negligible. Thus, Eqs. (10) and (12) tend to be correct and conventional isoconversional integral methods (KAS and OFW) lead to an accurate $E$ value closed to 80 kJ mol$^{-1}$ (Fig. 5). The $E$ values at $\alpha = 0.01$ are 80.88, 81.25, 80.70, 82.15 and 80.82 kJ mol$^{-1}$ respectively for NLN, FR, KAS, OFW and OFWC methods. On the contrary, this is not true at the end of the reaction. In this case the approximation of a constant $E$ value over $T_0$ and $T$ is not negligible and lead to an underestimation of $E_\alpha$ (conventional integral methods in Fig. 5). The $E$ values at $\alpha = 0.99$ are 119.80, 119.46, 115.32, 116.42 and 115.55 kJ mol$^{-1}$ respectively for NLN, FR, KAS, OFW and OFWC methods (reference 120 kJ mol$^{-1}$).

4.4. Application to experimental data

These computations were applied to an experimental case of the cure kinetics of an epoxy-amine system already presented [12] for the heating rates $\beta = 1$, 2 and 4 K min$^{-1}$. Note that the integration bounds were chosen in order to have a quasi-constant value of the reaction heat ($501.0 \pm 0.1$ J g$^{-1}$), according to the restrictions already highlighted in regard to the applicability of the FR method to transformations with temperature dependent reaction heat [25]. In spite of that, the $E_\alpha$-dependencies presented in Fig. 6 clearly show a systematic difference between NLN and other methods. This result may be perfectly explained in the light of the results obtained in this work in addition to those previously presented for the FR method [25]. As shown with simulated data, the difference between KAS, OFW, OFWC and NLN methods mainly starts from the hypothesis of a constant activation energy as postulated with conventional integral methods, while the difference between FR and NLN observed in the case of experimental data, derives from the use of instantaneous rate values (term $dH/ dt$ in Eq. (4)) as already explained [25].

4.5. Isothermal “predictions”

Kinetic computations are used for drawing mechanistic conclusions or for making simulations of the process. One of the most used simulation is called “isothermal predictions”, that means that non-isothermal data can be used to simulate the variation of the conversion degree ($\alpha$) vs. time ($t$) for a given (constant) temperature ($T_{iso}$). These kinds of simulations are
In order to avoid additional approximations, computation of the integral started at a temperature of 1 K using an integration step of 10−4 for both Eqs. (18) and (19). This was made in order to give a rigorous comparison of the various possibilities of evaluating the time t. Note that when conventional isoconversional methods are used (FR, KAS, OFW), an approximated form of p(x) is frequently used to perform iso thermal simulations. This equation was corrected by Flynn [35], who proposed to replace the term 88x with 86x. In the following, this equation will be referred as Eq. (20′). These two equations were also used to compute the conversion–time curves. In these cases the computation started at T = Tiso (here −20°C). The simulated isothermal curve, used as reference, was simulated according to the previously described procedure and integrated to yield the conversion vs. time data at a given Tiso.

### 4.6. Isoconversional methods

In the case of a single-step process, all the methods give very accurate results as seen in Table 1. The use of the Senum and Yang approximation for of p(x) (Eq. (20)) gives very similar results to those obtained using a numerical integration (Eq. (19)), while the correction

---

**Table 1**

<table>
<thead>
<tr>
<th>T/°C</th>
<th>Eq. no.</th>
<th>t98,DSC/ min</th>
<th>t98,NLN/ min</th>
<th>t98,FR/ min</th>
<th>t98,KAS/ min</th>
<th>t98,OFW/ min</th>
<th>t98,OFWC/ min</th>
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<tbody>
<tr>
<td>110</td>
<td>18</td>
<td>29.430 ± 0.01</td>
<td>29.435</td>
<td>29.434</td>
<td>29.434</td>
<td>29.835</td>
<td>29.464</td>
</tr>
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<td>20</td>
<td>20</td>
<td>29.489</td>
<td>29.489</td>
<td>29.453</td>
<td>29.852</td>
<td>29.513</td>
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<td>29.435</td>
<td>29.398</td>
<td>29.800</td>
<td>29.459</td>
<td></td>
</tr>
</tbody>
</table>

a t98,DSC: time to reach 98% conversion at the simulated DSC data.
b t98: time to reach 98% conversion at the temperature T obtained by the numerical procedure.

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In the following, this equation will be referred as Eq. (20). These two equations were also used to compute the conversion–time curves. In these cases the computation started at T = Tiso (here −20°C). The simulated isothermal curve, used as reference, was simulated according to the previously described procedure and integrated to yield the conversion vs. time data at a given Tiso.

### 4.6. Isoconversional methods

In the case of a single-step process, all the methods give very accurate results as seen in Table 1. The use of the Senum and Yang approximation for of p(x) (Eq. (20)) gives very similar results to those obtained using a numerical integration (Eq. (19)), while the correction
The conversion–time curves obtained in the case of a simulated complex mechanism are presented in Figs. 7, 8, 9 and 10 (some points were skipped for clarity) for two isothermal temperatures \(T_{iso} = 110\) and \(80\) °C and in Table 2 (\(T_{iso} = 110\) °C). These results where obtained using the \(E_a\)-dependencies computed for each method for the three heating rates \(\beta = 2, 5\) and \(10\) K min\(^{-1}\). Results presented in Table 2 show that the FR and NLN methods provide the more accurate values whatever the equation used for the computation of \(t\). The use of Eq. (19) or (20), gives more precise values with the integral methods of KAS, OFW and OFWC, while for NLN and FR the differences are negligible. The error is about 8, 7 and respectively 8% for KAS, OFW and OFWC at 98% conversion using Eq. (19). An additional interesting statement is that the Senum and Yang approximation (Eq. (20)) furnish very similar results to the numerical integration procedure (Eq. (19)) and can so be used in this case, if one does not have the possibility to perform more sophisticated programming. The correction proposed by Flynn (Eq. (20')) leads to exactly the same values as the numerical integration procedure (Eq. (19)) and can therefore be generalized. In fact, if the totality of the conversion–time curves are analysed (Figs. 8 and 9), it can be seen that Eq. (18) gives more accurate values for \(\alpha < 0.70\), while Eq. (19) is more accurate for \(\alpha > 0.70\). For long time prediction (i.e. lower isothermal temperature, \(T_{iso} = 80\) °C), the integral methods KAS, OFW and OFWC may lead to inaccurate results. The error is respectively 21, 17 and 20% for KAS, OFW and OFWC at 98% conversion using Eq. (19), and so the FR and NLN methods are more convenient.

In every case, the FR and NLN methods give more accurate results. Nevertheless, if just a simple estimation of the final time corresponding to \(\alpha = 99\)% is required, these results show that all the isoconversional methods give acceptable values.

The table below shows the comparison of the values obtained by simulation using Eq. (18) and by integration of the simulated DSC data.

<table>
<thead>
<tr>
<th>(T/°C)</th>
<th>(E_{iso})</th>
<th>(t_{iso,KAS})</th>
<th>(t_{iso,OFW})</th>
<th>(t_{iso,OFWC})</th>
</tr>
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<tbody>
<tr>
<td>110</td>
<td>18</td>
<td>106.674 ± 0.01</td>
<td>107.393</td>
<td>92.342</td>
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<td>107.393</td>
<td>107.941</td>
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<td>18</td>
<td>107.393</td>
<td>107.393</td>
<td>92.689</td>
</tr>
</tbody>
</table>

The results presented in Fig. 10 where obtained using the \(E_{iso}\)-dependency computed for the three heating rates 0.5, 2 and 5 K min\(^{-1}\) instead of 2, 5 and 10 K min\(^{-1}\). This figure clearly shows a better agreement between the simulated isothermal curve at 80 °C and the predicted conversion–time curves for each method. The use of lower heating rates to compute the \(E_{iso}\)-dependencies lead to more accurate predictions, probably because with lower heating rates, a better separation of the two individual reactions is obtained, as shown in Fig. 4.

5. Conclusions

Simulated data have clearly shown that, in the case of a complex reaction mechanism leading to a great variation of the effective activation energy on conversion, like it is often the case with experimental data, the approximation of a constant activation energy is the main source of error for integral methods. The major difference between differential and integral methods is not imputable to the approximations used for the temperature integral. In the case of simulated noisy data, usual integral methods are more stable for extreme values of the conversion degree. Nevertheless, the accuracy of all the methods can be easily improved using a simple smoothing algorithm. All the isoconversional methods gave accurate \(E\) values. Comparison of the \(E\)-dependencies obtained from experimental data, clearly show a systematic difference between Vyazovkin and other methods. This can be explained in the light of this work. In every simulated case, the results obtained with FR and NLN methods are very close and these methods give more accurate values. Because FR method employs instantaneous rate values it can be noise sensitive and its use is less suitable in the case of transformations with temperature dependent reaction heat. If the constancy of the activation energy is assumed for small segments, the NLN method does not present these drawbacks. Satisfactory isoconversional simulations for short time predictions were obtained with the presented methods. For long time predictions, the usual integral methods (KAS, OFW, OFWC) may lead to inaccurate results.

References
