

Isoconversional analysis of solid state transformations

A critical review. Part II. Complex transformations

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Abstract We will analyze the discrepancies between isoconversional methods when applied to complex transformations. The practical analysis of particular transformations leads us to conclude that (a) conventional integral methods based on integrated equations are essentially incorrect when dealing with variable activation energy; and (b) experimental inaccuracies and noise tend to give an apparent evolution of the energy variation, so that, non-constancy of the activation energy does not necessarily mean deviations from single-step transformations with constant activation energy.

Keywords Isoconversional methods · Activation energy · Thermal analysis · Solid-state transformations

Introduction

The second part of this review is devoted to the analysis of complex transformations. In particular, we will describe the use of the isoconversional methods introduced in the first part of this review (Part I [1]) to the case of non-constant heating rate and non-Arrhenius temperature dependence. To check the ability of the methods reviewed in Part I to deal with complex transformations, we have applied them to two different datasets: numerically simulated data from a complex transformation, and experimental data. The use of numerically simulated data is justified by the need to separate the effect of experimental noise and experimental artifacts from the inconsistencies related to method

inaccuracies or assumptions. Moreover, we will provide some piece of advice to manipulate experimental data to apply isoconversional methods properly.

Non-constancy of the activation energy

Originally isoconversional methods were based on the assumption that the system's state is defined exclusively by the degree of transformation, α . While this assumption is usually true for spatially homogeneous processes, for heterogeneous transformations, such as crystallization, it is only approximate [2]. For instance, one must expect deviations for

- (i) Heterogeneous transformations [2, 3];
- (ii) Complex mechanisms involving competing or independent processes [4–7];
- (iii) Transformations depending on parameters other than α and T (e.g., solid–gas reactions depend on the local gas partial pressure close to the sample [6, 8]).

To deal with more complex situations, isoconversional methods rely in the more general assumption that at a given degree of transformation, the transformation rate is also a function of α [9]:

$$\left[\frac{d \ln(dx/dt)}{dT^{-1}} \right]_{\alpha} = -\frac{E_{\alpha}}{R}. \quad (1)$$

where R is the gas constant, and E_{α} is the activation energy for this degree of transformation. Integration of Eq. 1 results in single-step transformations where the activation energy, E_{α} , and pre-exponential factor, A_{α} , depend on the degree of transformation. A variation of E_{α} with α corresponds to a variation of the microscopic energy barrier as the transformation proceeds (such an evolution is thought to occur during structural relaxation of amorphous

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materials [9, 10]). However, single-step transformations with variable E_α are scarce. In general, the non-constancy of E_α is related to complex transformations, i.e., transformations governed by several elementary processes. In this case, Eq. 1 holds approximately, the evolution of E_α with α is fictitious, and one cannot ascribe a physical meaning to the values of E_α unless there is some additional data in support of this assumption. Therefore, E_α must be interpreted in terms of an effective or apparent value.

In the derivation of all integral methods [1], it is assumed that E_α is constant, independent of α . Therefore, none of these methods is exact when E_α varies. Moreover, the integration assuming a constant value of E_α , smoothes the dependence of E_α on α . This source of inaccuracy does not apply to differential and advanced isoconversional methods, which are derived directly from Eq. 1.

Non-constant heating rate

Constant heating rate together with isothermal experiments are the most usual thermal history programmed in thermal analysis. However, the heat evolved during the transformation may result in noticeable deviations of sample's temperature from the programmed temperature [9]. Besides, some complex kinetic analyses combine constant heating rate and isothermal steps. Therefore, it is of practical interest to generalize isoconversional methods to hold under non-constant heating-rate conditions. From the methods presented in Part I, LT (Li-Tang), Fri (Friedman) and a-LT (advanced Li-Tang) are designed to work with an arbitrary variation of temperature. Besides, Vya (Vyazovkin) and a-Vya (advanced Vyazovkin) methods were originally derived to hold under non-constant heating-rate [9, 11]. As for Ortega's method, it can be easily generalized to hold under varying heating-rate conditions by replacing Eq. 20 in Part I by,

$$\Delta g_\alpha = A_\alpha \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left(-\frac{E_\alpha}{RT(t)}\right) dt \approx A_\alpha \exp\left(-\frac{E_\alpha}{RT_\alpha}\right) \Delta t_\alpha \quad (2)$$

where $\Delta t_\alpha \equiv t_\alpha - t_{\alpha-\Delta\alpha}$. Then, for an arbitrary temperature variation, Eq. 23 in Part I becomes

$$\ln \frac{1}{\Delta t_\alpha} - \ln \zeta'_{\text{Ort}}(t_\alpha) = -\frac{E_\alpha}{RT_\alpha} + \ln\left(\frac{A_\alpha}{\Delta g_\alpha}\right), \quad (3)$$

where $\zeta'_{\text{Ort}}(t_\alpha) \equiv \frac{\exp(x_\alpha)}{\Delta t_\alpha} \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left(-\frac{E_\alpha}{RT(t)}\right) dt$.

Non-Arrhenius temperature dependence

Non-Arrhenius behavior is observed in processes occurring on cooling conditions, such as crystallization of melts and

solutions [12–15] as well as gelation [16]. In these cases, the assumption that the rate constant is given by an Arrhenius dependence results in a fictitious evolution of E_α . Therefore, these processes cannot be analyzed with conventional integral methods. However, using advanced isoconversional methods and by considering the particular dependence of E_α on T , it is possible to determine the kinetic parameters [15, 16].

Alternatively, one can modify isoconversional methods to deal with a different dependence of the rate constant on temperature [13, 17]. Assuming that

$$k(T) = A \exp[-y(T)] \quad (4)$$

where $y(T)$ is a function of temperature, it can be demonstrated that [17]

$$g(\alpha) \approx -\frac{k(T_\alpha)}{\beta} \left[\frac{dy}{dT} \Big|_{T_\alpha} \right]^{-1}. \quad (5)$$

where $g(\alpha)$ is defined in Eq. 3 in part I. If the rate constant follows an Arrhenius behavior, $y(T) = E_\alpha/(RT)$, then Eq. 5 becomes,

$$g(\alpha) = \frac{T_{\alpha,i}^2 R}{\beta_i E_\alpha} A_\alpha \exp\left(-\frac{E_\alpha}{RT_{\alpha,i}}\right) \quad (6)$$

which is the KAS (Kissinger–Akahira–Sunose) relationship (Eq. 9 in part I).

For instance, Eq. 5 has been used [13, 17] to adapt KAS method [1] to analyze the solidification of a polymer where the rate constant is given by [12]

$$k(T) = A \exp\left(-\frac{B}{T(T_m - T)^2}\right) \quad (7)$$

where B is a constant and T_m is the melting temperature. In this case, Eq. 5 becomes

$$\ln\left(\frac{\beta_i(T_m - 3T_{\alpha,i})}{T_{\alpha,i}^2(T_m - T_{\alpha,i})^3}\right) = -\frac{B}{T_{\alpha,i}(T_m - T_{\alpha,i})^2} + \ln\left(-\frac{A f'(\alpha)}{B}\right) \quad (8)$$

where $f'(\alpha) = df(\alpha)/d\alpha$ and $f(\alpha)$ is the conversion function (Eq. 1 in part I). Thus, Eq. 5 can be used to modify KAS, c-KAS (corrected KAS), CC (Cai-Chen), and Ortega's methods [1].

Experimental data manipulation

To perform an isoconversional analysis, some numerical treatment has to be previously applied to the data obtained from thermal analysis techniques. These treatments are crucial: improper data manipulation could result in a significant loss of accuracy or systematic deviations from the

correct values. Despite their great importance, in general, little attention is paid to data manipulation details.

Generally speaking, the lesser the data manipulation, the more reliable the analysis. In particular, one should be very careful when applying smoothing filters since they can considerably alter the evolution of the measured property. Systematic smoothing should be avoided but when unavoidable, smoothed and raw data should be compared to prevent any data distortion. Since the evolution of solid-state transformations is quite smooth, Savitzky–Golay [18] filters are especially suited for thermal analysis data smoothing.

Whenever a baseline is to be subtracted, a certain degree of arbitrariness is always present in its selection. In the case of differential techniques, baseline subtraction is usually the most critical step, so it is essential to minimize that baseline correction. The baseline deviates from a zero line for two reasons: structural evolution of the sample and equipment imperfections. For instance, in the case of differential scanning calorimetry, the baseline deviations are mainly related to equipment asymmetries and to variations of the sample's heat capacity [19, 20]. For differential techniques, subtraction of a consecutive second measurement performed under identical conditions considerably minimizes the baseline deviations. Alternatively, one can subtract a blank experiment run under the same conditions.

Concerning the baseline shape, the most useful types are lines, integrals, and cubic splines. When the baseline deviations are mainly due to sample variation during the transformation, the best choice is an integral baseline. At a given temperature, the deviation of the baseline is taken as being proportional to the transformation degree. This baseline can be calculated iteratively: first an initial baseline is selected, and then the degree of transformation can be calculated. Afterward, a new baseline is calculated from the degree of transformation previously obtained. This process is repeated until the differences from two consecutive iterations are negligible. A cubic spline baseline represents a smooth and continuous slope change from the initial to the final transformation points. The cubic spline baselines consist of a cubic polynomial connecting the initial and final transformation points whose slope at the beginning and the end of the transformation coincides with the slope of the thermoanalytical curve at these points. To minimize the effect of the noise in the calculation of the initial/final slope, the best approach is to perform a linear interpolation along the interval where the evolution is flat just before/after the transformation begins/ends.

Afterward, the measured property is to be normalized to obtain either α or $d\alpha/dt$ as a function of the temperature. This normalization relies on the assumption that the measured thermal property is proportional to α or $d\alpha/dt$.

Alternatively, complex calibrations must be performed to determine α or $d\alpha/dt$.

Finally, interpolation methods are applied to obtain the temperature and transformation rate as a function of α . Given that the evolution of solid-state transformations is quite smooth, the best suited interpolation algorithm are the cubic spline [18]. It ensures that the interpolated data is smooth in the first derivative and continuous in the second derivative. Thus, the noise related to $d\alpha/dt$ is significantly reduced. As a consequence, the reliability of Friedman's and Li and Tang's methods is greatly improved.

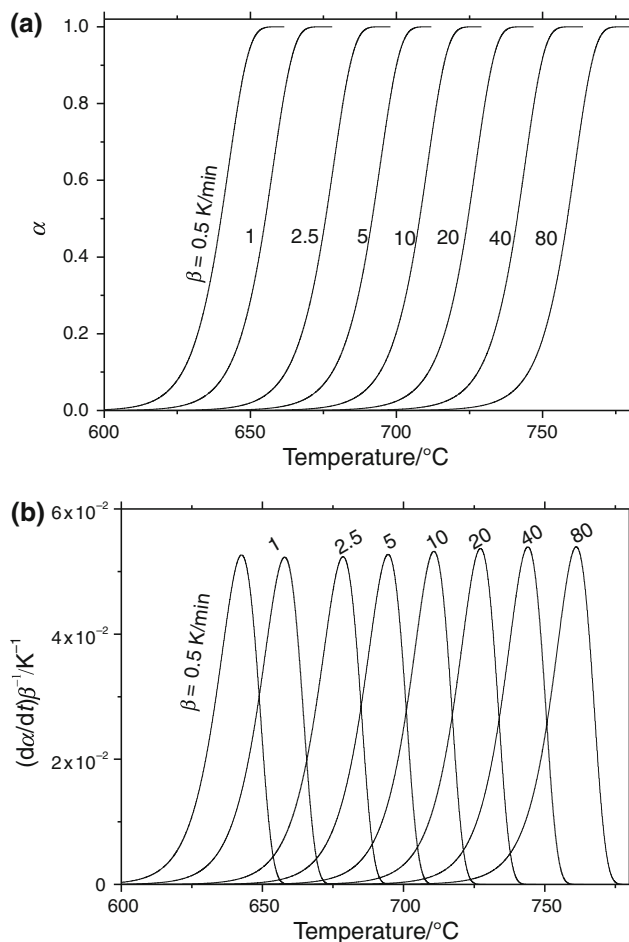
Complex transformation: crystallization with mixed nucleation mechanisms

To study the effect of a complex kinetics in isoconversional analysis and avoid confusion on with effects related to noise and other experimental uncertainties, we have chosen a numerical case. A literature review reveals that isoconversional methods have been tested mainly in complex chemical reactions involving competing or parallel processes (see [4, 11, 21–24]). In this section, we will analyze the crystallization driven by a mixture of nucleation mechanisms: a solid state transformation whose complex nature emerges from its inhomogeneous nature. In particular, we consider homogeneous nucleation plus the growth of pre-existing nuclei. The crystallization of amorphous silicon is usually controlled by homogeneous nucleation [25, 26]. However, the nucleation mechanism can be modified by introducing pre-existing nuclei, e.g., by ion implantation before isothermal annealing [27] or by pre-annealing the sample [28]. Furthermore, nucleation by both mechanisms has been observed in the crystallization of metallic glasses [29]. In the case of mixed nucleation, the kinetics cannot be described as a single-step transformation. Consequently, the apparent activation energy depends on the temperature and heating rate [30] and will exhibit a dependence on the degree of transformation.

Solid-phase crystallization is generally described by the Kolmogorov–Johnson–Mehl–Avrami (KJMA) theory [31–35]. The numerical recipe described in Ref. [36] has been used for calculating the evolution of the transformed fraction. In particular, we have chosen the parameters determined experimentally for the crystallization of amorphous silicon (summarized in Table 1) because both nucleation and growth rates can be described by an Arrhenius temperature dependence [25, 37]. In addition, we have assumed an initial nucleus density of $2 \mu\text{m}^{-3}$. This density of pre-existing nuclei makes a similar contribution from both nucleation mechanisms. Therefore, the observed kinetics exhibit a significant evolution of the activation energy during crystallization. The simulations have been

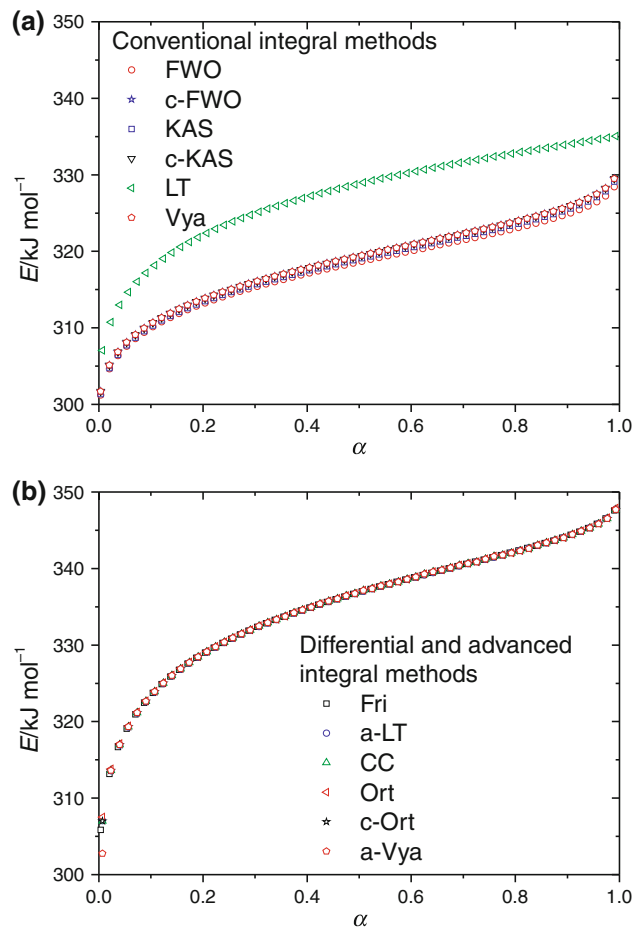
Table 1 Experimental parameters of amorphous silicon nucleation and growth rates [25]

Nucleation	Activation energy	511 kJ mol ⁻¹
	Pre-exponential term	1.7 × 10 ⁴⁴ s ⁻¹ m ⁻³
Growth	Activation energy	299 kJ mol ⁻¹
	Pre-exponential term	2.1 × 10 ⁷ m s ⁻¹

**Fig. 1** Evolution of the transformed fraction (a) and the transformation rate (b) for the numerical simulation of the crystallization of amorphous silicon when it is heated at different constant heating rates, β . An Arrhenius temperature dependence for the nucleation and growth rates has been assumed, and the corresponding parameters are summarized in Table 1. Moreover, three-dimensional growth and an initial nuclei density of 2 μm^{-3} has been assumed

run for eight different heating rates: $\beta = 0.5, 1, 2.5, 5, 10, 20, 40,$ and 80 K/min. The results are plotted in Fig. 1. It is noted that only one peak is observed despite the complex nature of the crystallization process.

Subsequently, we have applied the set of isoconversional methods described in Part I to determine the activation energy. The results are plotted in Fig. 2 and summarized in Table 2. To facilitate the comparison

**Fig. 2** Evolution of the activation energy with the degree of transformation derived from the isoconversional analysis of the crystallization of amorphous silicon (see Fig. 1)

between the methods, we have split the results into two plots: one for the conventional integral methods, and the other for the differential and advanced integral methods. From Fig. 2b, one can verify that all the differential and advanced integral methods give the same results: the differences in the mean value of E_x and the standard error of the mean value, SEM, values are, respectively, lower than 0.1 and 0.03 kJ/mol.

Let us now analyze E_x as crystallization proceeds. Since the growth of pre-existing nuclei is the main mechanism of the early stages of crystallization, one would expect that E_x tends to the activation energy of grain growth, E_G (299 kJ/mol, Table 1). From Fig. 2, this trend is clearly observed for $\alpha \rightarrow 0$. On the other hand, homogeneous crystallization becomes more important when α increases. The activation energy for homogeneous nucleation and three-dimensional growth, $E_H = (3E_G + E_N)/4 = 352$ kJ/mol [2], is higher than E_G . Consequently, E_x must increase with α , as observed in Fig. 2 for all isoconversional methods. In the case of differential and advanced integral methods, $E_x \rightarrow E_H$ when $\alpha \rightarrow 1$, indicating that homogeneous

Table 2 Mean value of the activation energy, \overline{E}_α ; standard error of the mean value, SEM; and mean number of iterations, \bar{n} , related to the isoconversional analysis of the crystallization of amorphous silicon plotted in Fig. 2

Method [1]	$\overline{E}_\alpha/\text{kJ mol}^{-1}$	SEM/ kJ mol^{-1}	\bar{n}
Fri	335.2153	0.47684	–
a-LT	335.2429	0.47203	–
a-Vya	335.2279	0.47369	–
CC	335.2422	0.47060	4.01
Ort	335.2920	0.46900	–
c-Ort	335.2422	0.47060	3.08

nucleation dominates in the last stages of the process. In contrast, the conventional integral methods fail to deliver this limiting value (Fig. 2a). In fact, they give a smoother evolution of E_α because, as commented previously, the temperature integral is solved by assuming constant activation energy from 0 to α . We conclude that for the particular transformation analyzed here, the conventional integral methods fail to deliver the correct evolution of E_α . Consequently, only the differential and advanced integral methods will be analyzed in the remainder of this subsection.

The very nice agreement between accuracy and reliability exhibited by a-LT, CC and corrected Ortega (c-Ort) differential methods [1] is noteworthy: the discrepancies in the calculated values of \overline{E}_α and SEM are less than 0.0007 and 1.4×10^{-3} kJ/mol, respectively. The method that shows the largest discrepancies is Ortega's method. However, the deviation in \overline{E}_α is 0.05 kJ/mol, an inaccuracy that is practically irrelevant.

From Table 2 we can conclude that the iterative method leading to the fastest convergence is the c-Ort method [1]. This faster convergence is due to the remarkable accuracy of the initial guess delivered by Ortega's method.

Experimental data: decomposition of CaCO_3

To deal with a real case, we have analyzed the thermogravimetric (TG) curves of the thermal decomposition of CaCO_3 . The experiments were carried out in a Mettler Toledo thermobalance model TGA851LF. Samples were placed in open alumina crucibles. A flow of 300 cm^3/min of high-purity nitrogen was kept constant inside the furnace. The initial mass was approximately 10 mg. The thermal decomposition behaves as a single-step reaction provided that the reverse reaction is prevented [4, 8, 38]. We have performed eight different measurements at heating rates ranging from 0.5 to 80 K/min. In Fig. 3, we have

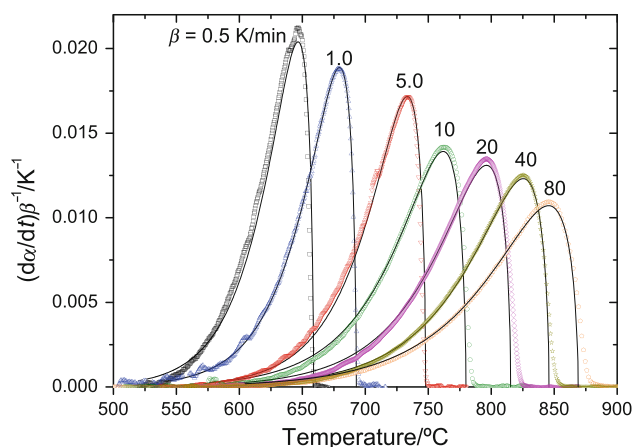


Fig. 3 Symbols are the evolution of the decomposition rate of CaCO_3 . The solid line is a fit to a single-step transformation following the procedure described in Ref. [38]. The reaction model is a n th-order rate reaction with $n = 0.42$. The activation energy is 189 kJ/mol

plotted the evolution of the transformation rate, which has been obtained directly from the first-time derivative of the TG signal normalized to the total mass change.

The isoconversional analysis of the two sets of experimental data is plotted in Fig. 4 and summarized in Table 3. For the sake of clarity, we have split the results into two graphs: one for conventional integral methods and the other for differential and advanced integral methods.

From Fig. 4b and Table 3, it can be seen that differential and advanced integral methods coincide. This nice coincidence is important because it also includes methods that are easier to implement: Friedman's, Ortega's, and a-LT methods [1]. The correct evolution obtained with Friedman's method weakens the objection concerning the detrimental influence of experimental noise on accuracy when compared to other isoconversional methods. This difficulty has been overcome thanks to the cubic spline interpolation algorithm used in the determination of T_i and $d\alpha/dt$ as a function of α . Concerning Ortega's method, the use of $\Delta\alpha$ being small enough (below 0.01) makes the inaccuracies negligible. Besides, one can always use the "corrected" Ortega method (see Part I) to improve accuracy. In fact, about three or four iterations do suffice to achieve an accuracy equivalent to the exact methods. Therefore, both Friedman's and Ortega's methods provide a simple and accurate way to determine E_α .

In contrast, the discrepancies between conventional integral methods are notorious (Fig. 4a; Table 3). Furthermore, when compared with the differential and advanced integral methods, E_α evolution is smoother. Consequently, we realize again, that the integral methods are unable to deliver reliable values of E_α . They are too inaccurate due to the approximation involved in their derivation, notably the constancy of E_α when doing the integration.

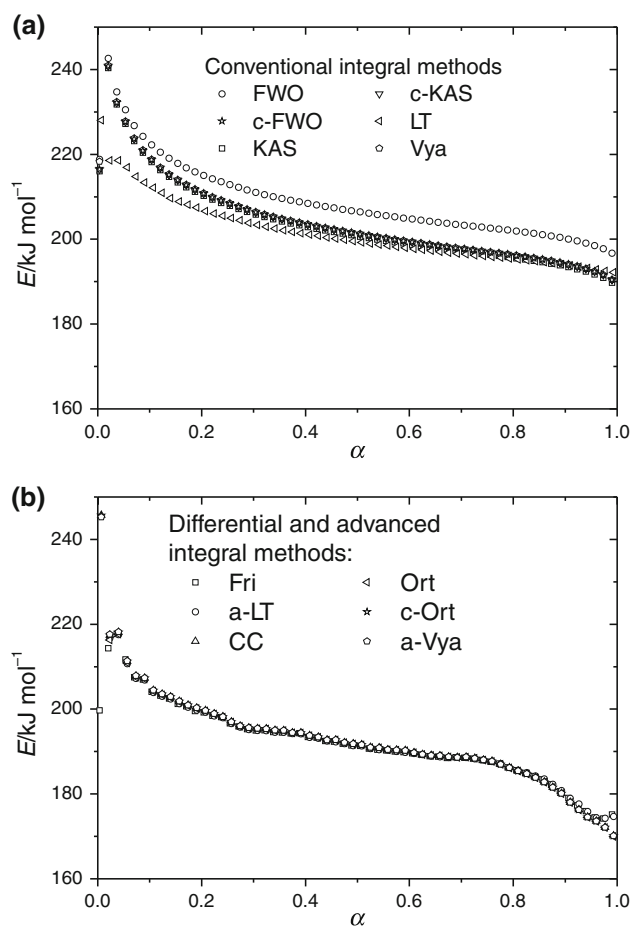


Fig. 4 Evolution of the activation energy with the degree of transformation derived from the isoconversional analysis of the decomposition of CaCO_3 (see Fig. 3)

Table 3 Mean value of the activation energy, \overline{E}_x , and number of iterations, \bar{n} , related to the isoconversional analysis of the thermal decomposition of CaCO_3 plotted in Figs. 3 and 4

Method [1]	$\overline{E}_x/\text{kJ mol}^{-1}$	SEM/ kJ mol^{-1}	\bar{n}
FWO	209.2634	0.56415	–
c-FWO	204.31527	0.62191	8
KAS	203.74269	0.62529	–
c-KAS	204.31527	0.62191	4.463
Vya	204.3659	0.6246	–
LT	201.3265	0.41364	–
Fri	192.2694	0.54424	–
a-LT	191.54647	0.72656	–
a-Vya	192.6468	0.63288	–
CC	192.61312	0.62923	4.124
Ort	192.54796	0.63413	–
c-Ort	192.61312	0.62923	3.290

The solid lines in Fig. 3 correspond to the predicted evolution obtained from the numerical calculation of a single-step kinetics of constant activation energy

($E = 189 \text{ kJ/mol}$). The simulated model is the n th-order reaction model. The fitting procedure is described in Ref. [38]. From Fig. 3, it is clear that the experimental data show nice agreement with a single-step kinetics of constant activation energy, i.e., in the temperature range analyzed, the reaction behaves as a single-step reaction. Therefore, one would expect a nearly constant value of E_x . In contrast, the analysis of the evolution of E_x plotted in Fig. 4b (or the standard error of the mean value, Table 3) exhibits a noticeable evolution of E_x . For instance, if we restrict the calculation to $0.2 < \alpha < 0.8$ to minimize the parasitic effects of low signal, we obtain a variation amplitude of 14 kJ/mol , i.e., $\Delta E/E \approx 3.6\%$. Therefore, apart from those cases where a remarkable evolution of E_x is observed, one cannot state the occurrence of complex transformations based only on the observed evolution of E_x .

Conclusions

The most commonly used and the most accurate isoconversional methods have been reviewed. All the isoconversional methods assume that the transformation rate is proportional to a conversion function related to the reaction model and to a rate constant that follows an Arrhenius temperature dependence. In the case of complex transformations or non-Arrhenius behavior, the activation energy delivered by isoconversional methods should be interpreted as effective or apparent activation energy.

Many isoconversional methods assumed isothermal or constant-heating temperature program. Li-Tang, Friedman, Vyazovkin, advanced Li-Tang, advanced Vyazovkin, and Ortega methods hold for an arbitrary temperature program.

As a general rule, conventional integral methods are to be avoided mainly because they are based on the very restrictive assumption that the apparent activation energy is constant. As a consequence, conventional integral methods fail to give a correct evolution of the apparent activation energy.

We have shown that, after proper numerical treatment of the experimental data, no appreciable differences can be observed between differential and advanced integral methods. Therefore, Friedman's and Ortega's methods provide a simple and reliable way to determine the activation energy.

Finally, non-constancy of the activation energy does not necessarily mean deviations from single-step transformations with constant activation energy. Experimental noise and artifacts could induce variations of the activation energy, which that would mask the actual nature of the transformation under study.

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