

Isoconversional analysis of solid state transformations

A critical review. Part I. Single step transformations with constant activation energy

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Abstract There are many mathematical methods to determine the activation energy from non-isothermal experiments. However, controversies arise over the different values obtained by these methods. We will show that the origin of these discrepancies is either inaccurate approximations of the so-called temperature integral or the occurrence of complex transformations. We will review and compare the most commonly used methods. For those methods that lack accuracy, we will introduce simple numerical modifications to make them exact. In addition, we will introduce a new method that allows easy and accurate determination of the activation energy.

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

Introduction

Many solid state transformations occur when a solid sample is heated. These transformations include physical processes such as melting, sublimation, and polymorphic transformation, and chemical processes. Thermal analysis denotes the experimental techniques that measure the evolution of a property when a sample is submitted to a controlled temperature program. Kinetic methods are designed to analyze thermal analysis data with the aim of characterizing the kinetics of solid state transformations.

Kinetic methods can be classified as model-fitting or model-free. While the first is based on the assumption that the transformation is ruled by a particular reaction model, the second allows the activation energies to be determined independently of the particular mechanism governing the transformation. Most of the model-free methods are isoconversional, i.e., they analyze the evolution of a given parameter at a given transformed fraction, α . Nowadays, there is common consensus that isoconversional (model-free) methods are the most reliable [1–7]. However, the results provided by the isoconversional methods should be interpreted carefully because erroneous conclusions regarding the nature of the mechanism governing the transformation can be reached easily.

In this article, we will review the most commonly used isoconversional methods. Some of them are quite inaccurate (for instance, see Ref. [6]). These inaccurate methods date from a time when thermal analysis equipment was quite inaccurate and computer-aided acquisition and numerical data processing capabilities were very limited or absent. Although some inaccurate methods are now obsolete, they are used too often. This could be related to the relatively complex implementation of some precise methods. We will introduce a simple numerical procedure to overcome the inaccuracies of approximate isoconversional methods. Moreover, we will introduce a new, simple, and accurate isoconversional method.

Isoconversional methods

Originally, isoconversional methods were based on the assumption that the rate of change in the state is a function of the state alone and the temperature and that the system state is described by a single parameter: the degree of

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transformation, α ($0 \leq \alpha \leq 1$). Under this assumption, the evolution of α can be described by a differential equation of the form [8, 9]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha), \quad (1)$$

where $f(\alpha)$ is the conversion function that depends on the reaction mechanism [8–10], and $k(T)$ is the rate constant. Equation 1 is known as the single-step kinetic equation.

Solid state transformations are usually thermally activated, and $k(T)$ follows an Arrhenius dependence [3, 4]:

$$k(T) = Ae^{-E/RT}, \quad (2)$$

where A is the pre-exponential factor, E is the activation energy, and R is the gas constant. For experiments carried out at a constant heating rate the explicit dependence on time of Eq. 1 can be eliminated with

$$\frac{d\alpha}{dT} = \frac{1}{\beta} Ae^{-E/RT} \cdot f(\alpha), \quad (3)$$

where $\beta \equiv dT/dt = \text{constant}$ is the heating rate. Upon integration over the variables α and T , one can easily obtain the evolution of α ,

$$g(\alpha) \equiv \int_0^\alpha \frac{du}{f(u)} = \frac{EA}{\beta R} p\left(\frac{E}{RT}\right), \quad (4)$$

where $p(x) \equiv \int_x^\infty \frac{\exp(-u)}{u^2} du$ is the temperature integral [10] (in Appendix 1, we provide some numerical and analytical recipes to evaluate $p(x)$). In the calculation of Eq. 4, it has been assumed that the initial temperature is low enough to neglect the initial transformation rate. The evolution of the transformation is given by

$$\alpha(T) = G\left(\frac{EA}{\beta R} p(x)\right), \quad (5)$$

where G is the inverse function for $g(\alpha)$, and $x \equiv E/(RT)$ is the reduced activation energy at temperature T . The expression of G for a number of reaction models is given in Refs. [11, 12]. Alternatively, in Appendix 2, we provide a simple numerical algorithm to compute G . Note that Eq. 5 provides a numerical solution for the calculation of the evolution of the transformed fraction for single-step transformations that is significantly more straightforward and accurate than the numerical integration of Eq. 3.

Applying isoconversional methods to continuous heating experiments relies on the determination of one or more of the system parameters (temperature, transformation rate,...) at which the same degree of transformation, α , has been reached for various heating rates, β . Then, activation energy for this degree of transformation, E_α , is obtained. Isoconversional methods can be classified into two categories: integral and differential [9].

Integral isoconversional methods

The integral methods are based on the integration of Eq. 3. Actually, except the method of Li and Tang, the integral methods are based on Eq. 4, and their accuracy is linked to the approximation used in the calculation of the temperature integral [6]. The methods of Li and Tang and Vyazovkin are noteworthy on their own because they are ‘exact’ in the sense that no numerical approximation has been made in their derivation.

Flynn–Wall–Ozawa’s method [13, 14] is based in Doyle’s approximation [15], which is one of the least accurate [6]

$$p(x) \approx \exp(-1.0518x - 5.330), \quad (6)$$

i.e., the dependence of $\ln[p(x)]$ on x is linear. If we substitute Eq. 6 into Eq. 4, we obtain

$$\ln \beta_i = -1.0518 \frac{E_\alpha}{RT_{\alpha,i}} - 5.33 + \ln\left(\frac{A_\alpha E_\alpha}{Rg(\alpha)}\right). \quad (7)$$

The subscript i denotes different heating rates. $T_{\alpha,i}$ is the temperature at which a degree of transformation, α , is reached while heating at a constant rate, β_i . Therefore, for a given α , the activation energy is obtained from the slope of the plot of $\ln \beta_i$ versus $1/T_{\alpha,i}$. Flynn [1] significantly improved the accuracy of the method by correcting the term -1.0518 by the actual slope of function $\ln[p(x)]$ at $x = E_\alpha/(RT)$, where \bar{T} is an average value over the temperature interval where the transformation takes place. In his original manuscript, Flynn introduced a table with the values of the slope of $\ln[p(x)]$ for $2 < x < 200$. Now, instead of using this table, one can easily calculate this slope as $\frac{1}{p(x)} \frac{e^{-x}}{x^2}$ (see Appendix 3).

The accuracy of Flynn–Wall–Ozawa’s method can be improved by iteration. Equation 7 becomes exact after introducing one additional term,

$$\ln \beta_i - \ln \zeta_{\text{FWO}}(x_{\alpha,i}) = -1.0518 \frac{E_\alpha}{RT_{\alpha,i}} - 5.33 + \ln\left(\frac{A_\alpha E_\alpha}{Rg(\alpha)}\right), \quad (8)$$

where $\zeta_{\text{FWO}}(x) \equiv p(x)/\exp(-1.0518x - 5.330)$ and $x_{\alpha,i} \equiv E_\alpha/RT_{\alpha,i}$. Equation 8 can be solved numerically by an iterative procedure:

- (i) obtain a first estimate of the activation energy assuming that $\zeta_{\text{FWO}}(x_{\alpha,i}) = 1$,
- (ii) from the previous estimation of the activation energy calculate $\ln \beta_i - \ln \zeta_{\text{FWO}}(x_{\alpha,i})$, and
- (iii) calculate a new estimate of the E_α from the slope of the plot of $\ln \beta_i - \ln \zeta_{\text{FWO}}(x_{\alpha,i})$ versus $1/T_{\alpha,i}$.

Steps (ii) and (iii) are to be repeated until the difference between two successive estimations of E_α are less than a chosen absolute value. The convergence of the iterative procedure is related to the accuracy of the first estimate, i.e., $\zeta_{\text{FWO}}(x) \approx 1$. Many authors have proposed other iterative methods to improve the accuracy [1, 2, 16, 17]. Although, these iterative methods can achieve high accuracy, only the method of Cai and Chen [18] is exact. Actually, the iterative method we have just proposed is a generalization of Cai and Chen’s method. As we will show, it can be applied to many approximate isoconversional methods.

The temperature integral $p(x)$ can be developed by an alternate series expansion [19]

$$p(x) = \frac{\exp(-x)}{x^2} \sum_{i=0}^{\infty} (-1)^i \frac{(i+1)!}{x^i}. \tag{9}$$

The Kissinger–Akahira–Sunose method [20, 21] is based on Murray’s approximation [22], which corresponds to the first term, $i = 0$, of Eq. 9 ($p(x) \approx \exp(-x)/x^2$). Under this approximation, for a given α , the activation energy is obtained from the slope of the plot of $\ln(\beta_i/T_{\alpha,i}^2)$ versus $1/T_{\alpha,i}$,

$$\ln \frac{\beta_i}{T_{\alpha,i}^2} = -\frac{E_\alpha}{RT_{\alpha,i}} + \ln \left(\frac{A_\alpha R}{E_\alpha g(\alpha)} \right). \tag{10}$$

The same approximation is applied to determine the E_α in the so-called Coats–Redfern method [10]. Equation 10 becomes exact by introducing the term $\zeta_{\text{KAS}}(x) \equiv x^2 p(x) / \exp(-x)$,

$$\ln \frac{\beta_i}{T_{\alpha,i}^2} - \ln \zeta_{\text{KAS}}(x_{\alpha,i}) = -\frac{E_\alpha}{RT_{\alpha,i}} + \ln \left(\frac{A_\alpha R}{E_\alpha g(\alpha)} \right). \tag{11}$$

Equation 11 can be numerically solved by following the iterative procedure previously described for the FWO method. Note that according to Murray’s approximation $\zeta_{\text{KAS}}(x) \approx 1$; therefore, the convergence of the iterative process is ensured by taking as the initial guess the activation energy given by the KAS method (Eq. 10).

To avoid inaccuracies, Vyazovkin proposed an exact method [23–25]. Under continuous heating conditions, E_α is determined from the minimum of function $\Phi(E_\alpha)$:

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j=1, j \neq i}^n \frac{\beta_j p(x_{\alpha,i})}{\beta_i p(x_{\alpha,j})}, \tag{12}$$

where the subscripts i and j identify the particular heating rate from the set of n measurements. A fast and accurate algorithm to minimize one-dimensional functions is provided by Brent’s algorithm [26], but using the first derivative [27]:

$$\frac{d\Phi(E_\alpha)}{dE_\alpha} = \sum_{i=1}^n \sum_{j=1, j \neq i}^n \frac{1}{E_\alpha} \frac{\beta_j p(x_{\alpha,i})}{\beta_i p(x_{\alpha,j})} \left(\frac{\exp(-x_{\alpha,j})}{x_{\alpha,j} p(x_{\alpha,j})} - \frac{\exp(-x_{\alpha,i})}{x_{\alpha,i} p(x_{\alpha,i})} \right). \tag{13}$$

The use of the derivative enhances the convergence rate and accuracy of the algorithm [27]. Besides, these algorithms require an initial interval of E_α to bracket the minimum. The KAS method is accurate enough to provide a starting to establish this interval.

Li and Tang’s [28, 29] method is obtained by taking logarithms on both sides of Eq. 1 and then integrating with respect to α :

$$\int_{\alpha_0}^{\alpha} \ln \left(\frac{d\alpha}{dt} \right)_{u,i} du = -\frac{E_\alpha}{R} \int_{\alpha_0}^{\alpha} \frac{1}{T_{u,i}} du + (\alpha - \alpha_0) \ln A + \int_{\alpha_0}^{\alpha} \ln f(u) du, \tag{14}$$

where α_0 is an initial transformed fraction (in their original work Li and Tang take $\alpha_0 = 0$). Therefore, from the slope of the plot of $\int_{\alpha_0}^{\alpha} \ln \left(\frac{d\alpha}{dt} \right)_{u,i} du$ versus $\int_{\alpha_0}^{\alpha} \frac{1}{T_{u,i}} du$ at a given α for a set of heating rates one can determine E_α . This method requires the determination of T and $d\alpha/dt$ at a fixed α for a given heating rate β_i . Compared to Vyazovkin’s method, LT’s method is easier to implement. However, its main drawback is that, at the beginning of the transformation, $d\alpha/dt \approx 0$ and the relative error related to $d\alpha/dt$ is significantly larger when compared to the rest of data. Thus, there is a large source of error in the calculation of $\ln(d\alpha/dt)$ in the first stages of the transformation which propagates to the calculation of E_α in the whole interval of α through the integral on the left hand side of Eq. 14. This problem can be partially solved by taking an initial transformed fraction, $\alpha_0 > 0$.

Other integral isoconversional methods proposed by Boswell [30] and Starink [6, 16] rely on the use of different approximations of $p(x)$. Those proposed by Starink are more accurate than the FWO and KAS methods. All these methods become exact when our iterative method is applied, i.e., when an additional term, $\zeta(x) \equiv p(x)/p_{\text{approx}}(x)$, is introduced in the exact same manner it has been done in Eqs. 8 and 11. The resulting equation can be solved iteratively.

Differential and advanced integral isoconversional methods

Differential isoconversional methods entail the experimental determination of the transformation rate (or a

parameter directly linked to the transformation rate) at different heating rates and a given α . The method of Friedman [31, 32] is exact because it does not use any approximation. Taking logarithms on both sides of Eq. 1, one obtains

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = -\frac{E_\alpha}{RT_{\alpha,i}} + \ln(A_\alpha f(\alpha)). \quad (15)$$

Therefore, at a given α , one can determine E_α from the slope of the plot of $\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i}$ versus $1/T_{\alpha,i}$ for a set of heating rates β_i . Like the LT method, Friedman's method requires the determination of temperature and $d\alpha/dt$ at a fixed α .

The main source of error in Friedman's method is inaccurate determination of the transformation rate. Indeed $d\alpha/dt$ is very sensitive to experimental noise [6, 33], especially for experimental techniques, such as thermogravimetry, that measure a parameter proportional to α . However, in our opinion, this point has sometimes been overemphasized, resulting in an unjustified discredit of Friedman's method. In fact, this source of error can be significantly reduced by the proper manipulation of experimental data [34].

Since integral methods are less sensitive to experimental noise [6, 35] but are inexact for variable E_α [34], a balanced alternative to the Friedman method consists in taking finite differences in an integral method. The partial integration provides robustness against experimental noise. In the limit of infinitesimal differences, these methods converge to the same value of E_α . In fact, we will see that the values of E_α obtained from these methods are virtually identical to those obtained from Friedman's method. These methods are known as advanced integral methods. In the following, we introduce some of these methods and will see that they can be directly derived from the integral methods previously introduced.

If we derive Eq. 14 with respect to α , we obtain Eq. 15, i.e., Friedman's method is the derivative counterpart of the integral LT method. We use finite differences, $\Delta\alpha$, in Eq. 14 to propose a new isoconversional method, 'advanced Li-Tang'. The advantage is clear: the method is exact but less sensitive to experimental noise thanks to the partial integration,

$$\int_{\alpha-\Delta\alpha}^{\alpha} \ln\left(\frac{d\alpha}{dt}\right)_{u,i} du = -\frac{E_\alpha}{R} \int_{\alpha-\Delta\alpha}^{\alpha} \frac{1}{T_{u,i}} du + \Delta\alpha \ln A + \int_{\alpha-\Delta\alpha}^{\alpha} \ln f(\alpha) du. \quad (16)$$

Hence, from the slope of the plot of $\int_{\alpha-\Delta\alpha}^{\alpha} \ln\left(\frac{d\alpha}{dt}\right)_{u,i} du$ versus $\int_{\alpha-\Delta\alpha}^{\alpha} \frac{1}{T_{u,i}} du$ at a given α one finds E_α .

To account for the dependence of E_α on α , Vyazovkin modified his integral method by limiting the integration to

a small interval of the transformed fraction $\Delta\alpha$ [35]. Under continuous heating conditions, E_α is determined from the minimum of function $\Omega(E_\alpha)$:

$$\Omega(E_\alpha) = \sum_{i=1}^n \sum_{j=1, j \neq i}^n \frac{\beta_j \Delta p(x_{\alpha,i})}{\beta_i \Delta p(x_{\alpha,j})}, \quad (17)$$

where

$$\Delta p(x_\alpha) \equiv \int_{x_\alpha}^{x_\alpha - \Delta\alpha} \frac{\exp(-u)}{u^2} du = p(E_\alpha/RT_\alpha) - p(E_\alpha/RT_{\alpha-\Delta\alpha}). \quad (18)$$

And its first derivative is

$$\frac{d\Omega(E_\alpha)}{dE_\alpha} = \sum_{i=1}^n \sum_{j=1, j \neq i}^n \frac{1}{E_\alpha} \frac{\beta_j [\Delta p(x_{\alpha,i})]}{\beta_i [\Delta p(x_{\alpha,j})]} \left(\frac{\exp(-x_{\alpha,j})}{x_{\alpha,j} \Delta p(x_{\alpha,j})} - \frac{\exp(-x_{\alpha,i})}{x_{\alpha,i} \Delta p(x_{\alpha,i})} \right). \quad (19)$$

We will label this method as a-Vya. It is worth noting that no approximation has been used in the derivation of Eq. 17. Therefore, this method is exact. Moreover, in Refs. [35, 36], it is shown for the numerical simulation of a complex transformation that a-Vya and Friedman methods deliver a practically identical value of E_α .

Cai and Chen [18] have proposed an iterative isoconversional method that is less computer time-consuming and simpler to implement than a-Vya. This method can be seen as the differential counterpart of the corrected KAS (c-KAS) method. By using finite differences in Eq. 4, we obtain the exact relationship,

$$\Delta g_\alpha \equiv g(\alpha) - g(\alpha - \Delta\alpha) = \frac{E A_\alpha}{\beta_i R} \Delta p(x_{\alpha,i}), \quad (20)$$

where $\Delta p(x_\alpha)$ is defined in Eq. 18. If we multiply Eq. 20 by $\exp(-x_\alpha)/x_\alpha^2$ and take the logarithm on both sides, we get

$$\ln \frac{\beta_i}{T_{\alpha,i}^2} - \ln \xi_{CC}(x_{\alpha,i}) = -\frac{E_\alpha}{RT_{\alpha,i}} + \ln \left(\frac{A_\alpha R}{E_\alpha \Delta g_\alpha} \right), \quad (21)$$

where $\xi_{CC}(x_\alpha) \equiv x_\alpha^2 \Delta p(x_\alpha) / \exp(-x_\alpha)$. Note the similarity between Eqs. 21 and 11 that accounts for the close link between the Cai and Chen and c-KAS methods. As with Eq. 11, Eq. 21 cannot be solved analytically but can be solved using the simple iterative procedure previously described. However, in this case and according to Murray's approximation, $\xi_{CC}(x) \approx \Delta\alpha$. Since the finite differences will usually be small (say $\Delta\alpha < 0.1$), one cannot take as an initial guess the result given by Eq. 21 under the approximation $\ln \xi_{CC}(x_{\alpha,i}) \approx 0$. It is surprising that in their original work Cai and Chen did not suggest any method to establish this initial guess. On the other hand, it can be easily shown that the assumption $\ln \xi_{CC}(x_{\alpha,i}) \approx 0$ will bring

an initial guess that coincides with the value of E_α delivered by the KAS method. Since varying E_α may produce differences in the estimation of E_α between integral and differential methods of over 20% [35], the convergence of the iterative method may be compromised by the accuracy of this initial guess.

The convergence of the Cai–Chen method can be improved using Ortega’s isoconversional method [33], which is obtained by taking the two first term of Taylor’s series expansion of $\Delta p(x_\alpha)$ in Eq. 20,

$$\ln \frac{\beta_i}{\Delta T_{\alpha,i}} = -\frac{E_\alpha}{RT_{\alpha,i}} + \ln \left(\frac{A_\alpha}{\Delta g_\alpha} \right), \tag{22}$$

where $\Delta T_{\alpha,i} \equiv T_{\alpha,i} - T_{\alpha-\Delta\alpha,i}$. This method becomes exact by adding the term $\ln \xi_{\text{Ort}}(x_{\alpha,i})$,

$$\ln \frac{\beta_i}{\Delta T_{\alpha,i}} - \ln \xi_{\text{Ort}}(x_{\alpha,i}) = -\frac{E_\alpha}{RT_{\alpha,i}} + \ln \left(\frac{A_\alpha}{\Delta g_\alpha} \right), \tag{23}$$

where $\xi_{\text{Ort}}(x_\alpha) \equiv \frac{E_\alpha}{R} \left(\frac{\Delta p(x_\alpha)}{\exp(-x_\alpha) \cdot \Delta T_\alpha} \right)$. Equation 23 can be solved iteratively. Since $\xi_{\text{Ort}}(x_{\alpha,i}) \approx 1$, an accurate initial guess can be obtained by assuming $\ln \xi_{\text{Ort}}(x_{\alpha,i}) \approx 0$. Indeed, as we will see, Ortega’s method is the most accurate among the approximate ones, and in the iterative resolution of Eq. 23 Ortega’s corrected method is the one that achieves faster convergence.

The methods presented are summarized in Table 1. In the next section, we will analyze their accuracy and convergence.

Results and discussion

The analysis of single-step transformations reveals intrinsic inaccuracies in the isoconversional methods related to the approximations used in their derivation. The models used

in this analysis are summarized in Table 2 and cover most of the common kinetic models. Since virtually all solid state transformations take place for $8 < E/(RT) < 100$ [6, 37–41], we will limit the analysis of the accuracy to this interval of the reduced activation energy. To work with realistic parameters, we have limited the values of the activation energy to the interval $50 < E < 400$ kJ/mol and temperature to the range between 25 and 700 °C (a range accessible for most thermal analysis techniques). The pre-exponential term, A , has been chosen to fit the transformation ranges to these limits. The A values vary between 10 and 10^{42} 1/s. To perform the isoconversional analysis, we have calculated the evolution of the transformed fraction for eight different heating rates: $\beta = 0.5, 1, 2.5, 5, 10, 20, 40,$ and 80 K/min. To calculate the evolution of the transformed fraction, we have used Eq. 5. The accuracy was of the order of the numerical precision of floating point numbers ($\sim 10^{-16}$). No interpolation procedure has been used to obtain the values of the different variables ($T, d\alpha/dt, \dots$) at a given transformation degree. Instead, we have determined these parameters numerically to remove any influence of the interpolation step in the accuracy analysis. Finally, we have evaluated E_α for 298 equidistant values of α . Thus, $\Delta\alpha = 1/299$ and the minimum and maximum values of α are $\Delta\alpha$ and $1 - \Delta\alpha$, respectively.

We have analyzed 92 sets of data. Each dataset consists of eight thermograms related to a given transformation model, A and E values. In Fig. 1, we have plotted the evolution of E_α given by different isoconversional methods for one particular set of data. For each set of data, we have evaluated the mean value of the activation energy, $\overline{E_\alpha}$, the deviation from the exact value, $\Delta E = E - \overline{E_\alpha}$, and the standard error of the mean value (SEM). As expected, all the ‘exact’ methods give a constant value of E_α (typically $\text{SEM} < 10^{-10}$ kJ/mol), which virtually coincides with the

Table 1 Summary of the isoconversional methods analyzed

Method	Label	Eq. no.	Accuracy	Classific.	Reference
Flynn–Wall–Ozawa	FWO	7	Approx.	Integral	[13, 15]
Corrected FWO	c-FWO	8	Exact	Integral	This study
Kissinger–Akahira–Sunose	KAS	11	Approx.	Integral	[20, 21]
Corrected KAS	c-KAS	12	Exact	Integral	This study
Vyazovkin	Vya	14	Exact	Integral	[23–25]
Li–Tang	LT	16	Exact	Integral	[28, 29]
Friedman	Fri	17	Exact	Differential	[31]
Advanced Li–Tang	a-LT	18	Exact	Advanced int.	This study
Advanced Vyazovkin	a-Vya	19	Exact	Advanced int.	[35]
Cai–Chen	CC	23	Exact	Advanced int.	[18]
Ortega	Ort	24	Approx.	Differential	[33]
Corrected Ort.	c-Ort	25	Exact	Advanced int.	This study

The term ‘exact’ refers to the fact that no approximation has been made in the derivation of the method from Eqs. 1 or 4

Table 2 Set of reaction models used in the calculation of single-step transformations (Figs. 2, 3, and 4)

Model	$f(\alpha)$	$g(\alpha)$
n -dimensional reaction, $R(n)$	$(1 - \alpha)^{n-1/n}$, $n = 1, 2$, or 3	$n[1 - (1 - \alpha)^{1/n}]$
Kolmogorov–Johnson–Mehl–Avrami, $KJMA(n)$	$n \cdot (1 - \alpha) \cdot [-\ln(1 - \alpha)]^{n-1/n}$	$[-\ln(1 - \alpha)]^{1/n}$
Mampel, 1st order, F1	$(1 - \alpha)$	$[-\ln(1 - \alpha)]$
2nd order, F2	$(1 - \alpha)^2$	$\frac{1}{1-\alpha} - 1$
1D diffusion, D1	$(2\alpha)^{-1}$	α^2
2D diffusion, D2	$1/[-\ln(1 - \alpha)]$	$(1 - \alpha) \ln(1 - \alpha) + \alpha$
3D diffusion, Jander's, D3	$\frac{3(1-\alpha)^{2/3}}{2[1-(1-\alpha)^{1/3}]}$	$[1 - (1 - \alpha)^{1/3}]^2$
3D diffusion, Ginstling and Brounshtein, D4	$\frac{3}{2} [(1 - \alpha)^{-1/3} - 1]^{-1}$	$1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3}n$

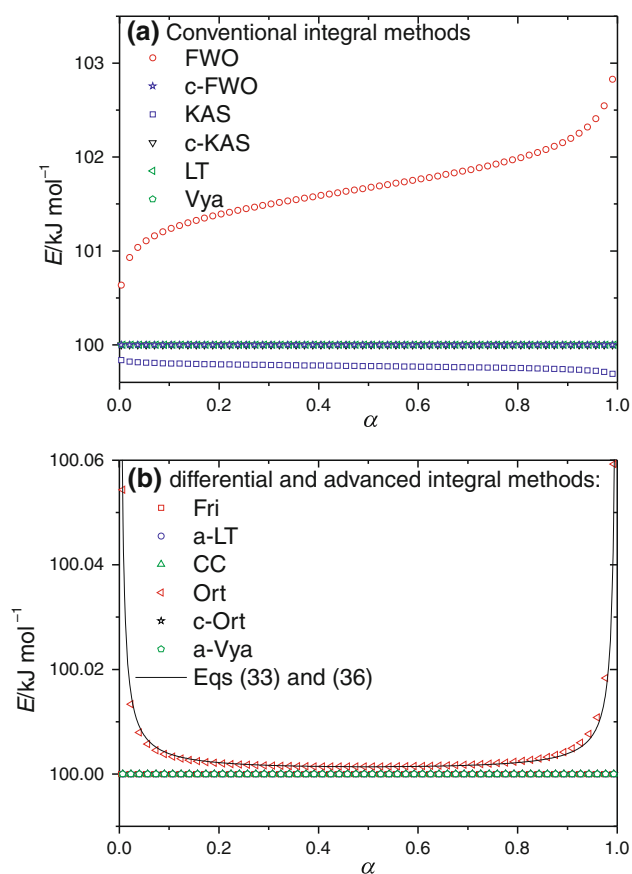


Fig. 1 Plot of the activation energy with respect to the degree of transformation delivered by the isoconversional methods summarized in Table 1 for a single-step process. Parameters: $E = 100$ kJ/mol, $A = 5 \times 10^6$ 1/s, and the reaction model is the second-order transformation, F2 (see Table 2). The solid line in **b** corresponds to the approximate value of E determined from Eqs. 33 and 36 assuming that the exact value is 100 kJ/mol

exact value (ΔE is typically less than 10^{-12} kJ/mol). Still, we have observed slight differences between methods. The best accuracies were obtained for the iterative methods (c-FWO, c-KAS, CC, and c-Ort) and the Friedman method.

Regarding the convergence of the iterative methods, none of them fail, so the initial guesses proposed in this manuscript are reliable. However, the convergence rate depends on the accuracy of the initial guess. The iterative process was repeated until the difference in the activation energy between two consecutive iterations was less than 10^{-10} kJ/mol. As expected, the c-FWO method exhibits the worst convergence since the initial guess given by the FWO is the least accurate (typically about eight iterations are necessary to complete the iterative process). Since the accuracy of the initial guess depends on the reduced activation energy at a given temperature x (see Appendix 3), the rate of convergence also depends on x . For instance, the c-Ort method, which is the one that exhibits the fastest convergence, requires less than five iterations for $x > 20$ (that increases to six for $x = 8$). On the other hand, the CC iterative method shows a slightly slower convergence rate than c-Ort. (As we have noted, the troubles in the selection of the initial guess for the CC method are to be expected for complex transformations.) Finally, the c-KAS method presents a slower convergence rate: for $x > 20$ the maximum number of iterations is six (five or four iterations are typically necessary to complete the iterative process) and up to eight iterations are needed for $8 < x < 20$.

The accuracy of the approximate methods is still controversial [42, 43]. It is clear that their accuracy is directly linked to that of the approximation used in the calculation of the temperature integral [6]. Although some authors have addressed the relationship between the accuracy of E_α and the accuracy of the temperature integral (a relevant contribution is given by Orfao [44]), as far as we know, no one has paid attention to the relationship between the accuracy of E_α and the reaction model. We have evaluated the relative error of E_α for 92 sets of single-step transformations given by ten different reaction models. The results of these analyses are summarized in Figs. 2, 3, and 4 for the FWO, KAS, and Ortega methods, respectively. Since

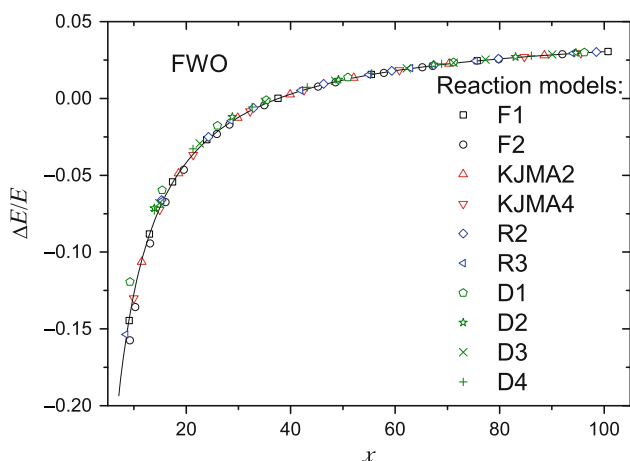


Fig. 2 Plot of the relative error in the calculation of the activation energy versus the reduced activation energy at a given temperature for the Flynn–Wall–Ozawa isoconversional method. The calculation has been done for ten different reaction models (see Table 2). The reduced activation energy is determined from the peak temperature of the transformation rate evolution obtained when the system is heated at a constant rate of 5 K/min. The *solid line* corresponds to the prediction of the relative error given by Eqs. 33 and 34

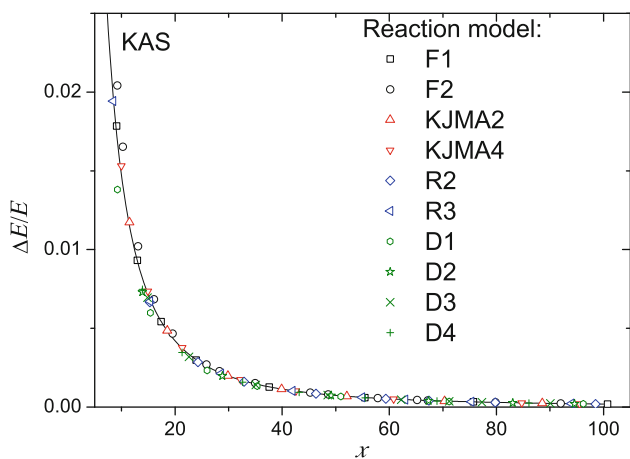


Fig. 3 Plot of the relative error in the calculation of the activation energy versus the reduced activation energy at a given temperature for the Kissinger–Akahira–Sunose isoconversional method. The calculation has been done for ten different reaction models (see Table 2). The reduced activation energy is determined from the peak temperature of the transformation rate evolution obtained when the system is heated at a constant rate of 5 K/min. The *solid line* corresponds to the prediction of the relative error given by Eqs. 33 and 35

the accuracy is directly linked to the reduced activation energy at a given temperature, x [6, 44], we have plotted the evolution of the relative error versus x . Given that the transformations take place in a temperature range, the value of x is not constant in the α range where E_α is computed. The value of x taken for the plots in Figs. 2, 3, and 4 corresponds to a representative temperature: the peak temperature for the transformation rate evolution obtained upon heating at a constant rate of 5 K/min. The previous

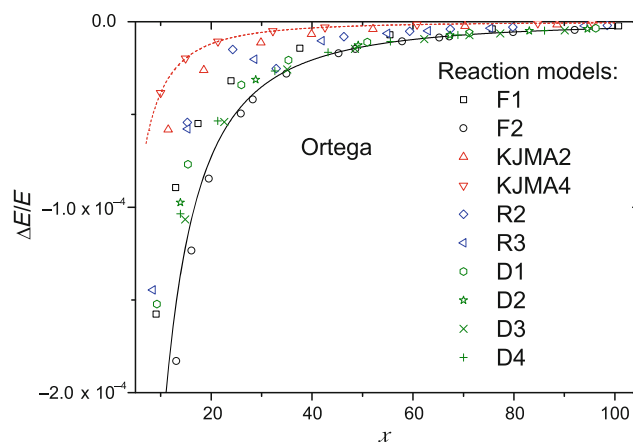


Fig. 4 Plot of the relative error in the calculation of the activation energy versus the reduced activation energy at a given temperature for Ortega’s isoconversional method. The calculation has been done for ten different reaction models (see Table 2). The reduced activation energy is determined from the peak temperature of the transformation rate evolution obtained when the system is heated at a constant rate of 5 K/min. The *solid line* corresponds to the prediction of the relative error given by Eqs. 33 and 36 for the F2 (*solid*) and KJMA4 (*dashed*) reaction models

assumption does not represent a significant limitation because the variations in x are relatively small [10, 12].

From Figs. 2, 3, and 4, we can conclude that the relative error related to the FWO and KAS methods is independent of the reaction model, while for Ortega’s method it is significantly dependent on the reaction model. This result agrees with the prediction given by our theoretical analysis of the relative error developed in Appendix 3. We have plotted the predicted evolution of the relative error for the KAS, FWO, and Ortega methods as solid lines in Figs. 2, 3, and 4, respectively. Since for Ortega’s method the relative error also depends on the reaction model, we have plotted the expected evolution of the relative error for two models, the KJMA4 and F2 models, which exhibit the smallest and largest error, respectively. The agreement between the observed error and the theoretical predictions is excellent. This nice agreement verifies the validity of our theoretical analysis of the relative error.

According to our analysis (see Eq. 36), the relative error of Ortega’s method also depends on α . Indeed, since for most reaction models the product $f(\alpha) \cdot g(\alpha)$ tends to vanish for $\alpha \rightarrow 0,1$, the relative error diverges for $\alpha \rightarrow 0,1$. In Fig. 1b, we have plotted the evolution of the error for Ortega’s model calculated from the numerical data (symbols) and from Eq. 36 (solid line). As can be seen, the evolution predicted for the error agrees with the actual evolution. Since the error determined from the numerical data corresponds to the deviations between the actual evolution and the average value of E_α , to account for this dependence on α , the solid lines plotted in Fig. 4 correspond to the integration of (Eq. 36) from $\Delta\alpha$ to $1 - \Delta\alpha$.

From the y -scales of Figs. 2, 3, and 4, it is evident that the most accurate method by far is Ortega's and we confirm [6] that the FWO method is the least accurate one. This result is consistent with the c-Ort method having the fastest convergence rate and the c-FWO method having the slowest one. Therefore, Ortega's method provides the best initial guess for differential iterative methods. Conversely, because of the relatively small error related to the KAS method, it provides a correct initial guess for integral methods. However, a faster convergence rate and a more reliable guess for iterative integral methods can be obtained from a more accurate integral method, for instance the one developed by Starink [6].

Finally, we have compared SEM and ΔE_z values. In all kinetics, for KAS and FWO methods, SEM values are significantly smaller than ΔE , meaning that the variation of E_z with α is not representative of the actual deviations from the exact value. This conclusion is apparent in Fig. 1.

Conclusions

The most commonly used and the most accurate isoconversional methods have been reviewed. We have introduced a new simple and accurate advanced integral isoconversional method that is the counterpart of the Li and Tang method.

We have analyzed the accuracy of the approximate methods in determining the activation energy. We have shown that the inaccuracy of Ortega's model is in practice negligible (relative error $< 2 \times 10^{-2}\%$). The relative error of KAS method ($< 2\%$) is not relevant for the analysis of most experiment. Conversely, the relative error of FWO method can be as high as 15%. We have also introduced an iterative procedure that turns approximate methods into exact ones.

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Appendix 1. Calculation of the temperature integral

The temperature integral,

$$p(x) \equiv \int_x^\infty \frac{\exp(-u)}{u^2} du, \quad (24)$$

is related to the exponential integral function [17] $Ei(x)$ according to

$$p(x) = \frac{\exp(-x)}{x} + Ei(-x). \quad (25)$$

Some scientific software includes the calculation of the function $Ei(x)$. It can also be easily calculated from its

series expansion [19]. For a complete review of different approximations to evaluate the temperature integral see Ref. [44]. An approximation that combines accuracy and simplicity is the fourth-order Padé approximant [45, 46]

$$p(x) \approx \frac{\exp(-x)}{x} \times \left(\frac{x^3 + 18x^2 + 86x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \right) \quad (26)$$

The absolute error of Eq. 26 is less than 1.4×10^{-11} for $x > 8$ (this corresponds to a relative error of 3×10^{-6}). As pointed out by several authors [6, 46, 47], in their original work, Senum and Yang [45] erroneously quoted a coefficient. However, some authors still use the incorrect Padé approximant. We have derived the sixth-order Padé approximant which gives an absolute error less than 1.3×10^{-13} for $x > 8$ (this corresponds to a relative error of 4×10^{-8}):

$$p(x) \approx \frac{\exp(-x)}{x} \times \left(\frac{x^5 + 40x^4 + 552x^3 + 3168x^2 + 7092x + 4320}{x^6 + 42x^5 + 630x^4 + 4200x^3 + 12600x^2 + 15120x + 5040} \right). \quad (27)$$

For $x > 12$, the absolute error is less than 10^{-16} , i.e., it is negligible for double precision computer calculations.

Appendix 2. Calculation of the function G

For most of the reaction models in Table 2, function G has an analytical solution [11, 12]. For those cases, where no analytical solution is available we have developed a numerical recipe. G is the inverse function for $g(\alpha)$,

$$\alpha = G(z) \Leftrightarrow g(\alpha) = z. \quad (28)$$

Our goal is to calculate α for a given z . The transformation rate can be obtained from the first derivative of Eq. 5

$$\frac{d\alpha}{dt} = \frac{dG}{dz} \frac{dz}{dt} = k(T)G'(z), \quad z \equiv \frac{EA}{\beta R} p\left(\frac{E}{RT}\right). \quad (29)$$

If we compare Eq. 28 to Eq. 1, we obtain:

$$f(\alpha) = \frac{dG}{dz}. \quad (30)$$

And from the Taylor series expansion of function G we get

$$G(z) \approx G(z_0) + G'(z_0)(z - z_0). \quad (31)$$

If we substitute Eqs. 29 and 30 into Eq. 31, we obtain the iterative solution

$$\alpha_{i+1} \approx \alpha_i + f'(\alpha_i)(z - g(\alpha_i)). \quad (32)$$

Some care has to be taken in the choice of the initial guess to ensure the convergence of the iterative process. However, this task is quite simple since G is a monotonically increasing function and $0 \leq G(z) \leq 1$.

Appendix 3. Accuracy of the FWO, KAS, and Ortega isconversional methods

For the FWO method, the activation energy, E_α , is obtained from an approximate linear relationship between $\ln \beta_i$ and the reduced temperature at a given transformation degree $x_{\alpha,i} = E_\alpha/(RT_{\alpha,i})$ (Eq. 7). Then, E_α is obtained directly from the slope of the plot of β_i versus the reciprocal of the temperature. One can estimate the relative error in the determination of E_α , by comparing the value delivered by the approximate method to the value corrected by the slope of the exact relationship,

$$\frac{\Delta E_\alpha}{E_\alpha} = 1 - \frac{m_{\text{exact}}}{m_{\text{approx}}}, \tag{33}$$

where m_{exact} (m_{approx}) is the slope of the plot of $\ln \beta_i$ versus $x_{\alpha,i}$ for the exact (approximate) relationship. Actually, our determination of the relative error is based on the estimation of the exact result given Flynn's correction [1] but generalized to several approximate methods. From Eq. 7, $m_{\text{approx}} = -1.0518$ while m_{exact} can be deduced from Eq. 8:

$$\begin{aligned} m_{\text{exact}} &= -1.0518 + \frac{d}{dx_{\alpha,i}} \ln \xi_{\text{FWO}}(x_{\alpha,i}) \\ &= -\frac{1}{p(x_{\alpha,i})} \frac{\exp(-x_{\alpha,i})}{x_{\alpha,i}^2}. \end{aligned} \tag{34}$$

Following the same procedure, one can estimate the relative error determination of E_α for the KAS methods through Eq. 33. For the KAS method $m_{\text{approx}} = -1$ (Eq. 10), and m_{exact} is obtained from Eq. 11:

$$m_{\text{exact}} = -1 + \frac{d}{dx_{\alpha,i}} \ln \xi_{\text{KAS}}(x_{\alpha,i}) = -\frac{1}{\xi_{\text{KAS}}(x_{\alpha,i})} + \frac{2}{x_{\alpha,i}}. \tag{35}$$

Likewise for Ortega's method $m_{\text{approx}} = -1$ (Eq. 22) and from Eq. 23 one obtains

$$\begin{aligned} m_{\text{exact}} &= -1 + \frac{d}{dx_{\alpha,i}} \ln \xi_{\text{Ort}}(x_{\alpha,i}) \\ &= -1 + \frac{1}{2f(\alpha)g(\alpha)} \left[1 - \frac{p(x_{\alpha,i})x_{\alpha,i}^2}{\exp(-x_{\alpha,i})} \left(1 + \frac{2}{x_{\alpha,i}} \right) \right]. \end{aligned} \tag{36}$$

In the derivation of Eq. 36, we have to approximate ξ_{Ort} by its third-order Taylor series expansion. Note that Ortega's

method is based on the same series expansion but up to the second order:

$$\xi_{\text{Ort}}(x_\alpha) \approx 1 + \frac{1}{2} \frac{R}{E_\alpha} x_\alpha^2 \Delta T_\alpha \approx 1 + \frac{1}{2} \frac{\Delta \alpha}{f(\alpha)g(\alpha)} \frac{p(x_{\alpha,i})x_{\alpha,i}^2}{\exp(-x_{\alpha,i})}. \tag{37}$$

The second term in Eq. 37 is obtained taking into account that $\Delta \alpha \approx (d\alpha/dT)\Delta T$ and substituting Eqs. 3 and 5.

From Eqs. 34 and 35, one can state that the accuracy of FWO and KAS methods depends exclusively on the reduced activation energy at a given temperature, x , while for Ortega's method, Eq. 36, the accuracy also depends on the reaction model and the finite differences, $\Delta \alpha$. Indeed, the smaller $\Delta \alpha$, the smaller the relative error. This leads to a significantly better accuracy for Ortega's method when compared to FWO and KAS.

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