Isoconversional analysis of solid-state transformations

A critical review. Part III. Isothermal and non isothermal predictions

J. Farjas · P. Roura

Abstract A key issue in kinetic analysis is the "prediction" of the evolution of a solid state transformation for a particular temperature program. Many methods have been proposed to calculate this evolution from kinetic parameters determined from non-isothermal isoconversional methods. In this study, we will review and compare the most accurate methods. We will then introduce a new method that provides an accurate prediction for an arbitrary temperature program.

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

Introduction

Kinetic methods are routinely employed to determine the kinetic parameters of solid-state transformations from thermal analysis experiments. In particular, there are isoconversional methods which are model-free, i.e., they allow the activation energies to be determined independently of the particular mechanism governing the transformation. Isoconversional methods rely on data obtained from experiments performed at different constant temperatures (isothermal) or different heating rates (non-isothermal). There is a common agreement that isoconversional methods are among the most reliable kinetic methods [1–8]. Apart from the conclusions that can be drawn from the mechanisms involved in solid-state transformations, kinetic methods are especially suitable for predicting the evolution of the transformation when the sample is submitted to a particular temperature program [9–11]. These predictions are useful for industrial purposes [7, 12] and for designing more efficient thermal treatments.

This article is the last of a series of the three devoted to reviewing isoconversional methods. In the first article [13], we analyzed the accuracy of isoconversional methods, whereas in the second article [14], we studied their application in complex transformations. The present article is devoted to reviewing the most common and accurate methods that predict the evolution of a solid-state transformation from the kinetic parameters obtained from non-isothermal isoconversional methods, i.e., "model-free" prediction methods. To this purpose, we will apply them to experimental and numerical data. Moreover, we will introduce a new method which is exact within the validity of the isoconversional principle. This method can predict the evolution of the transformation when submitted to an arbitrary temperature program.

Isoconversional principle

Isoconversional methods are based on the assumption that the rate of change in the state is a function of the state itself and the temperature, and that the system state is described by a single parameter: the degree of transformation, α ($0 \leq \alpha \leq 1$). Accordingly, the transformation rate is given by:

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

where $k(T)$ is the rate constant and $f(\alpha)$ is the conversion function which is related to the reaction mechanism [15–17]. Equation 1 is known as the single-step kinetic equation. In general, in solid-state transformations, the rate constant, $k(T)$, is adopted from the Arrhenius law [3, 4]:

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

where A is the pre-exponential factor, E is the activation energy, and R is the gas constant.

For experiments performed at a constant heating rate, Eq. 1 can be integrated:

$$g(\alpha) \equiv \int_0^\alpha \frac{du}{f(u)} = \frac{EA}{\beta R} p\left(\frac{E}{RT}\right), \tag{3}$$

where $\beta \equiv dT/dt = $ constant, which is the heating rate, and $p(x) \equiv \int_x^\infty \frac{\exp(-u)}{u^2} du$, which is the temperature integral [18] (in Ref. [13] we provide some numerical recipes for calculating the temperature integral).

Conventional isoconversional methods are known as integral methods because they are based on the integration of Eq. 1. Indeed, most integral methods are based on Eq. 3. In the derivation of all the integral methods [5], it is assumed that E is independent of α. This assumption is in contrast with the dependence of E on α (E_α) observed in many practical situations. The integration assuming a constant value of E_α, smoothes the dependence of E_α on α, i.e., integral methods fail to deliver the correct evolution of E_α [2, 3, 19]. To account for this dependence, differential and advanced isoconversional methods rely on the more general hypothesis (*isoconversional principle*) that, at a given degree of transformation, the transformation rate is also a function of α [19],

$$\left[\frac{d\ln(d\alpha/dt)}{dT^{-1}}\right]_\alpha = -\frac{E_\alpha}{R}. \tag{4}$$

Integration of Eq. 4 results in single-step transformations where both the activation energy, E_α, and pre-exponential factor, A_α, depend on the degree of transformation,

$$\frac{d\alpha}{dt} = A_\alpha \exp\left[-\frac{E_\alpha}{RT}\right] f(\alpha). \tag{5}$$

Moreover, and in contrast to integral methods, differential and many other advanced methods can be applied to non-constant heating rate experiments [19] and non-Arrhenius temperature dependence of the rate constant [20, 21].

Isothermal and non-isothermal predictions

Model-free predictions are calculated using kinetic parameters obtained from non-isothermal isoconversional analysis, i.e., experiments carried at different heating rates β_i. Non-isothermal experiments are preferred [3] because they are more easily and more rapidly performed, and they allow a wider temperature range to be explored [22]. Isoconversional methods rely on the determination of the temperature, $T_{\alpha,i}$, at which a degree of transformation, α, is reached while heating at a constant rate, β_i (some methods also require the determination of the transformation rate $(d\alpha/dt)_{\alpha,i}$ [23, 24]. The result of the isoconversional analysis is N discrete data sets, α_j and E_j, where E_j is the activation energy at a given degree of transformation, α_j. The step employed in the discretization of α is $\Delta\alpha = \alpha_j - \alpha_{j-1} = 1/(N-1)$. In addition, integral methods provide $g(\alpha_j)$ whereas differential and advanced methods deliver $A_{\alpha j}f(\alpha_j)$ (advanced methods deliver $\frac{A_{\alpha_j}}{\Delta g_{\alpha_j}} \equiv \frac{A_{\alpha_j}}{g(\alpha_j)-g(\alpha_{j-1})} \approx \frac{A_{\alpha_j}f(\alpha_j)}{\Delta\alpha}$) [13].

Vyazovkin [25] has developed a method for isothermal predictions based on Eq. 3 which is exact for single-step transformations with constant activation energy. The time, t_j needed to reach a degree of transformation, α_j at a constant temperature, T_{iso} is given by,

$$t_j = \left[\beta_i \exp\left(-\frac{E_j}{RT_{iso}}\right)\right]^{-1} \int_0^{T_{j,i}} \exp\left(-\frac{E_j}{RT}\right) dT$$
$$= \frac{E_j}{R\beta_i} \frac{p\left(E_j/(RT_{j,i})\right)}{\exp\left(-E_j/(RT_{iso})\right)}, \tag{6}$$

where $T_{j,i}$ is the temperature at which α_j is reached while heating at a constant rate, β_i. An advantage of this method is that the pre-exponential factor A_α, which improves accuracy and robustness, is not used [3]. Since Eq. 6 is obtained when assuming constant activation energy, the most suitable isoconversional method for determining E_j is an integral method.

Vyazovkin's method assumes that E_j is independent of α in the whole integration interval. As a consequence, in the case of complex transformations, one should expect deviations from the actual behavior [26]. Vyazovkin [27] partially solved this problem by taking into account the dependence of E_α on α during the non-isothermal measurement:

$$t_j = \left[\exp\left(-\frac{E_j}{RT_{iso}}\right)\right]^{-1} \sum_{k=1}^{N} \int_{t_{k-1}}^{t_k} \exp\left(-\frac{E_k}{RT(t)}\right) dt \tag{7}$$

However, this method neglects the dependence of E_α on α during the isothermal transformation. This is probably the

reason why Eq. 7 does not lead to more accurate predictions than Eq. 6 in the case of complex transformations [26]. We have overcome this limitation by taking into account the dependence of E_α on α during the isothermal transformation:

$$t_j = t_{j-1} + \frac{E_j}{R\beta_i} \frac{p(E_j/(RT_{j,i})) - p(E_j/(RT_{j-1,i}))}{\exp(-E_j/(RT_{iso}))}. \quad (8)$$

Equation 8 is exact within the framework of the isoconversional hypothesis, Eq. 4.

The methods presented above are restricted to isothermal predictions. However, it is of practical interest to be able to predict the evolution of the transformation for an arbitrary temperature program to work with more realistic conditions and to be able to design more complex heat treatments. Our method can be modified to work for an arbitrary temperature program $T(t)$:

$$t_j = t_{j-1} + \frac{E_j}{R\beta_i} \left[p\left(\frac{E_j}{RT_{j,i}}\right) - p\left(\frac{E_j}{RT_{j-1,i}}\right) \right]$$
$$\left[\int_{t_{j-1}}^{t_{j-1}} \exp\left(-\frac{E_j}{RT(t)}\right) dt \right]^{-1}. \quad (9)$$

Equations 8 and 9 are exact within the isoconversional hypothesis, so the more appropriate choice to determine E_j is a differential or advanced isoconversional method.

Roduit et al. [12] have also developed an exact isothermal method which is based directly on Eq. 5:

$$t_j = t_{j-1} + \int_{\alpha_{j-1}}^{\alpha_j} \frac{d\alpha}{[Af(\alpha)]_j \exp(-E_j/(RT_{iso}))} dT, \quad (10)$$

where $[Af(\alpha)]_j$ is $A_\alpha f(\alpha)$ for $\alpha = \alpha_j$. To apply this method, a differential or advanced isoconversional method is required to determine $[Af(\alpha)]_j$. The method of Roruit et al. can be easily adapted to work with an arbitrary program by time discretization, Δt, of the temperature program $T(t)$. At each time step, $\alpha(t + \Delta t) = \alpha(t) + d\alpha/dt|_{\alpha(t)} \Delta t$, and the transformation rate can be easily determined from Eq. 5 using the parameters obtained from the isoconversional analysis, e.g., using an interpolation algorithm [28] to determine the particular values of $A_\alpha f(\alpha)$ and E_α at a given $\alpha(t)$:

$$\alpha(t + \Delta t) = \alpha(t) + A_\alpha f(\alpha) \exp\left(-\frac{E_\alpha}{RT(t)}\right) \Delta t. \quad (11)$$

In fact, Eq. 11 comes directly from the isoconversional hypothesis; the transformation rate is a function of α. Isoconversional methods allow us to determine the transformation rate at a given α, Eq. 5. Therefore, the evolution of the transformation is obtained directly from the time integration of the transformation rate.

It is noted that Eq. 11 calculates $\alpha(t)$ where time t follows the temperature program discretization, whereas Eq. 9 gives the time required to reach a transformation degree α_j, i.e., it follows the discretization employed in the isoconversional analysis.

To check the accuracy of the methods described above, we have applied them to three different data sets: a numerically simulated data set from various single-step transformations with constant E_α; two numerically simulated data sets from complex transformations; and experimental data. The use of numerically simulated data set is justified by the need to separate the effect of experimental noise and experimental artifacts from the inconsistencies related to inaccuracies or assumptions in the method.

Numerical data: single step transformations with constant activation energy

The models analyzed in this article are summarized in Table 2 of Ref. [13] and cover most of the common kinetic models. The details of the numerical calculations and isoconversional analyses are given in Ref. [13]. We have evaluated E_α for $N = 1000$ equidistant values of α ($\Delta\alpha = 1/999$). To determine the kinetic parameters, we have employed the Friedman method [29].

As expected, Vyazovkin's methods, Eqs. 6 and 7, and our method, Eq. 8, deliver identical isothermal predictions since they are all exact and equivalent for single-step transformations with constant activation energy. Moreover, the agreement between the isothermal predictions and the
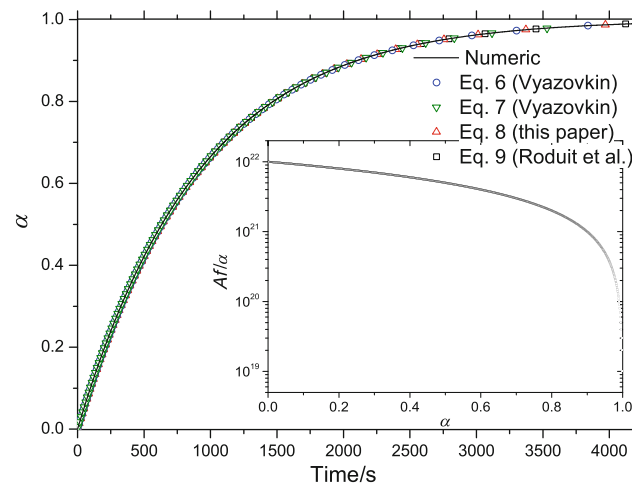
Fig. 1 *Solid line*: Numerical evolution of the transformed fraction for a first-order transformation ($f(\alpha) = 1 - \alpha$) and constant temperature (250 °C). Parameters: $E = 250$ kJ mol^{-1}, $A = 10^{22}$ s^{-1}. *Symbols*: isothermal predictions (for the sake of clarity only one out of every 13 points is plotted). *Inset*: Determination of the $A_\alpha f(\alpha)$ parameter from Friedman's isoconversional analysis
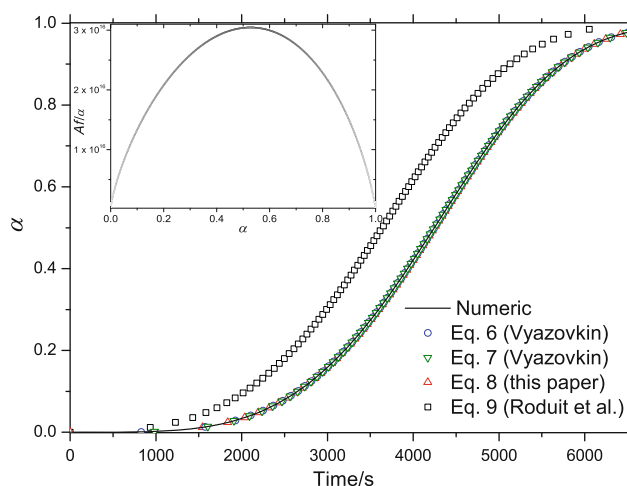
Fig. 2 *Solid line*: Numerical evolution of the transformed fraction for a KJMA transformation $\left(f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{n-1/n}\right)$ with $n = 4$ and constant temperature (250 °C). Parameters: $E = 200$ kJ mol^{-1}, $A = 10^{16}$ s^{-1}. *Symbols*: Isothermal predictions (for the sake of clarity only one out of every 13 points is plotted). *Inset*: determination of the $A_\alpha f(\alpha)$ parameter from Friedman's isoconversional analysis

calculated evolution is excellent, as shown in Figs. 1 and 2 (discrepancies in the value of α are of the order of 10^{-12} or less). More examples are given in the Electronic supplementary material.

The same agreement is obtained with Eq. 10, for the first-order reaction model (see Fig. 1). Conversely, in the case of the Kolmogorov–Johnson–Mehl–Avrami model, KJMA, there is a time shift between the actual evolution and the prediction (see Fig. 2). This result is unexpected because the method of Roduit et al. is also an exact method. In fact, the method of Roduit et al. provides an accurate prediction for all the models analyzed except for the KJMA model. Broadly speaking, reaction models can be classified into two groups: "deceleratory" models, in which the highest isothermal transformation rate occurs at the beginning of the reaction; and "acceleratory or sigmoid" models, in which the highest isothermal rate occurs at an intermediate stage of transformation [30]. The KJMA model belongs to the second group, while the other reaction models analyzed belong to the first group. This difference in behavior corresponding to a different evolution of the function, $f(\alpha)$; in the deceleratory models, $f(\alpha)$ is a monotonic decreasing function while for the KJMA model, $f(\alpha)$ vanishes at the beginning and at the end of the transformation, $\alpha = 0$ and 1, and has a maximum somewhere in between. As a consequence, the parameter $A_\alpha f(\alpha)|_{\alpha=0}$ vanishes in the KJMA model while it remains positive in the other models (see inset in Figs. 1, 2). Roduit's method is based on the determination of $A_\alpha f(\alpha)$, thus, in the first stages—and using the KJMA model—the prediction is very sensitive to inaccuracies in the determination of $A_\alpha f(\alpha)$ ($A_\alpha f(\alpha)$ is determined from the intercept of

Friedman plot, and is very sensitive to inaccuracies). Moreover, for constant heating rate experiments, the transformation rate vanishes at the beginning of the transformation, which means that inaccuracies in the determination of kinetic parameters grow when $\alpha \to 0$. In fact, non-isothermal isoconversional methods fail to deliver $A_\alpha f(\alpha)$ and E_α when $\alpha = 0$. It is noted that despite the fact that we are analyzing precise numerical data, even very small uncertainties in the determination of $A_\alpha f(\alpha)$ when $\alpha \to 0$ will result in a significant error in the first stages of the isothermal predictions. Equation 10 gives the time interval related to $\Delta\alpha$, therefore, the error in the calculation of time in the first stages yields a time shift for the whole prediction (see Fig. 2). Hence, Eqs. 10 and 11 are sensitive to the inaccuracies in the determination of $A_\alpha f(\alpha)$ at the first stages of the transformation and fail to give an exact prediction for sigmoid reactions. To minimize this effect, we have extrapolated the value of $A_\alpha f(\alpha)$ for $\alpha = 0$. This procedure has been applied to the prediction plotted in Fig. 2. We have observed a significant reduction of the time shift. However, deviations are still noticeable as can be seen from Fig. 2. Moreover, when dealing with experimental data, it is crucial to have a proper construction of the baseline to minimize the error in the determination of the kinetic parameters in the first stages of the transformation [7, 12, 31].
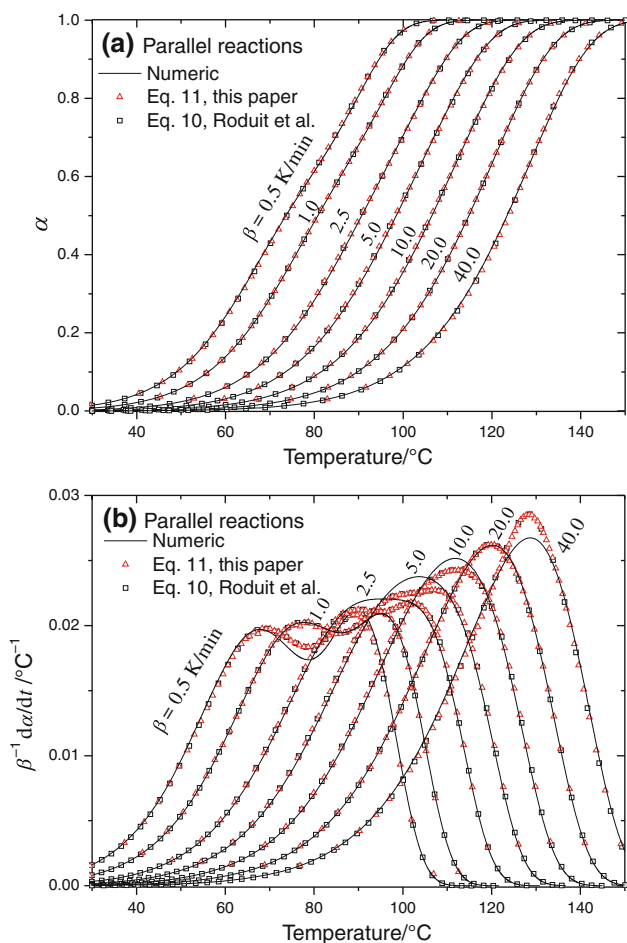
Numerical data: parallel reactions

One numerical model that can be employed to analyze complex kinetics involves the overlapping of two parallel reactions [2, 26]. Specifically, we have analyzed two equally weighted first order reactions:

$$\frac{d\alpha_i}{dt} = A_i \exp\left[-\frac{E_i}{RT}\right](1-\alpha_i), \quad i = 1, 2 \text{ and}$$

$$\alpha = \frac{1}{2}(\alpha_1 + \alpha_2), \tag{12}$$

where $E_1 = 80$ kJ mol^{-1}, $A_1 = 10^{10}$ min^{-1}, $E_2 = 120$ kJ mol^{-1}, and $A_2 = 10^{15}$ min^{-1}. To calculate the evolution of the transformed fraction, we have used a fifth-order Runge–Kutta method with adaptive step-size control [28] (the absolute and relative tolerances have been set to 10^{-12}). The simulations were carried out for seven different heating rates: $\beta = 0.5, 1, 2.5, 5, 10, 20,$ and 40 K min^{-1}. The results are plotted in Fig. 3.

Vyazovkin stated that in the case of parallel reactions, the effective activation energy depends on both the temperature and the degree of transformation [8, 11]. Owing to this dependence on temperature, the isoconversional hypothesis is an approximation. To check the goodness of this hypothesis, we have calculated the evolution of the

Fig. 3 *Solid line*: Evolution of the transformed fraction (**a**) and the transformation rate (**b**) for the numerical simulation of a parallel reaction, Eq. 12, when it is heated at several heating rates, β. *Symbols*: Non-isothermal predictions (for the sake of clarity only one out of every 50 points is plotted)
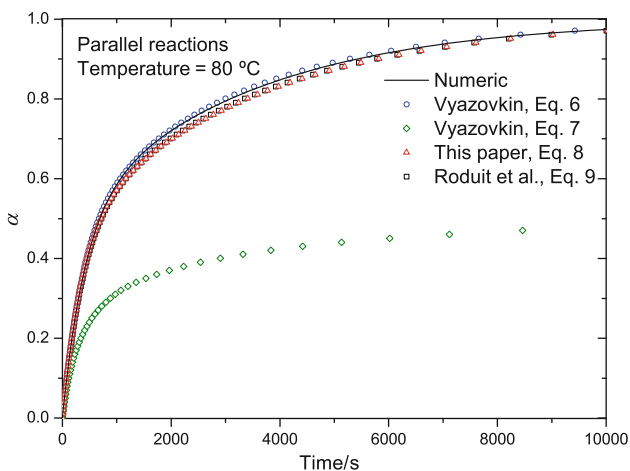
Fig. 4 *Solid line*: Evolution of the transformed fraction for the numerical simulation of a parallel reaction, Eq. 12, when it occurs at a constant temperature of 80 °C. *Symbols*: Isothermal predictions (for the sake of clarity only one out of every 10 points is plotted)

transformation using the non-isothermal prediction methods described previously in the Eqs. 9 and 11. In particular, we have assumed linear variations of the temperature, i.e., we have used the same temperature program as in the numerical calculations. The results are plotted as symbols in Fig. 3. Figure 3a shows a good agreement between the non-isothermal predictions and the actual evolution. However, small deviations of the predictions are apparent with the transformation rate curves in Fig. 3b. Thus, although the isoconversional hypothesis is not exact, it is very accurate. In addition, we have found that the predictions yielded by Eqs. 9 and 11 are virtually identical. It is as we expected because they are both exact methods within the isoconversional hypothesis, and in contrast with the models in the previous section, this reaction model is based on two parallel first order reactions, therefore, the term $A_\alpha f(\alpha)$ does not vanish when $\alpha \rightarrow 0$. As a consequence, no time shift is expected when applying the method of Roduit et al. (Eq. 11).

In Fig. 4, we have plotted the isothermal prediction delivered by different methods. We applied Friedman's method [29] to obtain the kinetic data used for the predictions of Eqs. 8 and 10, whereas Vyazovkin's integral method [32–34]) was applied to obtain them for the prediction of Eqs. 6 and 7[1] (the details of the numerical methods used in the isoconversional analyses are given in Ref. [13]). With the exception of Eq. 7, all methods provide an accurate prediction. Surprisingly, the best prediction is obtained from the approximate method of Eq. 6. However, this trend is not systematic and varies depending on the particular temperature analyzed (for more examples, see the Electronic supplementary material). In any case, this particular result shows that, for this complex transformation, the deviations of the actual transformation with respect to the isoconversional hypothesis are more relevant than the inaccuracies within the isoconversional hypothesis. Equation 7, on the other hand, is inferred by assuming a constant activation energy for the isothermal transformation and a non-constant activation energy for the non-isothermal transformation. As evidenced in Fig. 4, this inconsistency may result in very large inaccuracies. Therefore, in the following section, we will avoid using this method.

Numerical data: crystallization with mixed nucleation mechanisms

In this section, we will analyze a solid-state transformation whose complex nature emerges from its inhomogeneous

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[1] Like Sbirrazzuoli et al. [26], we have not observed significant differences when using the integral method in place of the differential or advanced methods and vice versa.

nature, i.e., crystallization driven by a mixture of nucleation mechanisms (homogeneous nucleation plus pre-existing nuclei). In this case, the assumption of the isoconversional hypothesis is also an approximation.
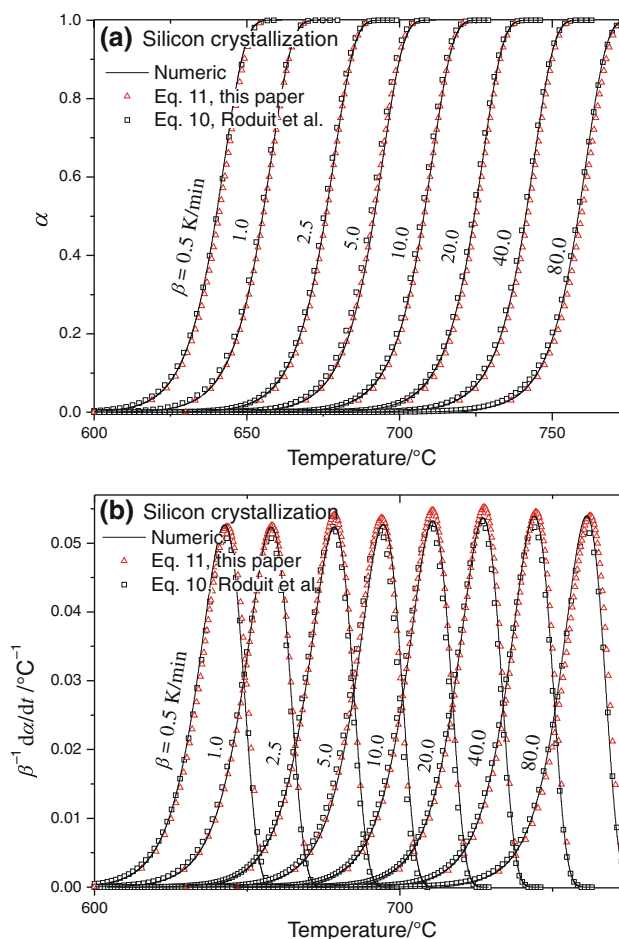
The crystallization of amorphous silicon is usually controlled by homogeneous nucleation [35, 36]. However, the nucleation mechanism can be modified by introducing pre-existing nuclei [37, 38]. Furthermore, nucleation by both mechanisms has been observed in the crystallization of metallic glasses [39]. In the case of mixed nucleation, the kinetics cannot be described as a single-step transformation [14, 40].

Solid-phase crystallization is generally described by the KJMA theory [41–45]. We have used the numerical recipe described in Ref. [46] to calculate the evolution of the transformed fraction. Experiments show that nucleation and growth rates obey an Arrhenius temperature dependence [35, 47]. For the numerical calculation, we have chosen the parameters determined experimentally for the crystallization of amorphous silicon (Table 1). In addition, we have assumed an initial nuclei density of 2 μm^{-3} which corresponds to a similar contribution from both nucleation mechanisms. The simulations have been run for eight different heating rates: $\beta = 0.5, 1, 2.5, 5, 10, 20, 40$, and 80 K min^{-1}. The results are plotted in Fig. 5.

As in the previous case, there is a good agreement between the non-isothermal predictions and the actual evolution. However, in contrast to the previous case, the predictions obtained from Eqs. 9 and 11 do not match. This is because, in this case, the term $A_\alpha f(\alpha)$ does vanish when $\alpha \to 0$. Therefore, a time shift is expected for the prediction given by Eq. 11. In any case, discrepancies between both the methods are very small and it is difficult to state which method delivers the more accurate prediction. Therefore, in this case, the intrinsic inaccuracy of the method of Roduit et al. is insignificant—a conclusion that is confirmed by the isothermal prediction (see Fig. 6), where one can observe small differences between the method of Roduit et al. and the other methods. Moreover, as in the previous example, there is a nearly perfect match between Eq. 6, which is approximate, and Eq. 8 which is exact. This result confirms that, for complex transformations, the approximations employed in the derivation of the methods from the isoconversional hypothesis are of little importance.

Table 1 Experimental parameters of amorphous silicon nucleation and growth rates [35]

Nucleation	Activation energy	511 kJ/mol
	Pre-exponential term	1.7×10^{44}/s/m^3
Growth	Activation energy	299 kJ/mol
	Pre-exponential term	2.1×10^7 m/s

Fig. 5 *Solid line*: 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 several heating rates, β. *Symbols*: Non-isothermal predictions (for the sake of clarity only one out of every 20 points is plotted)
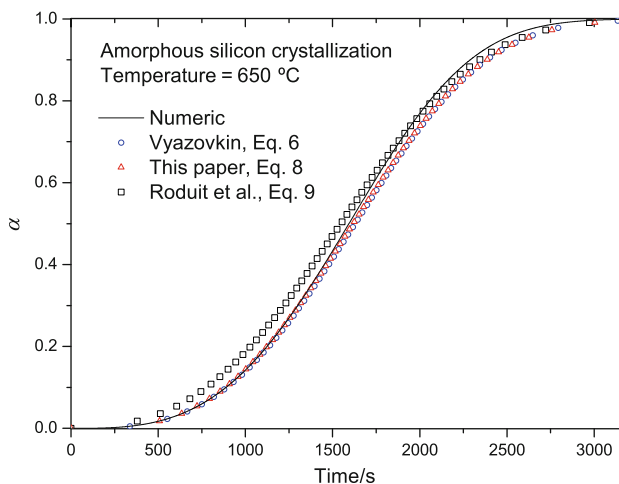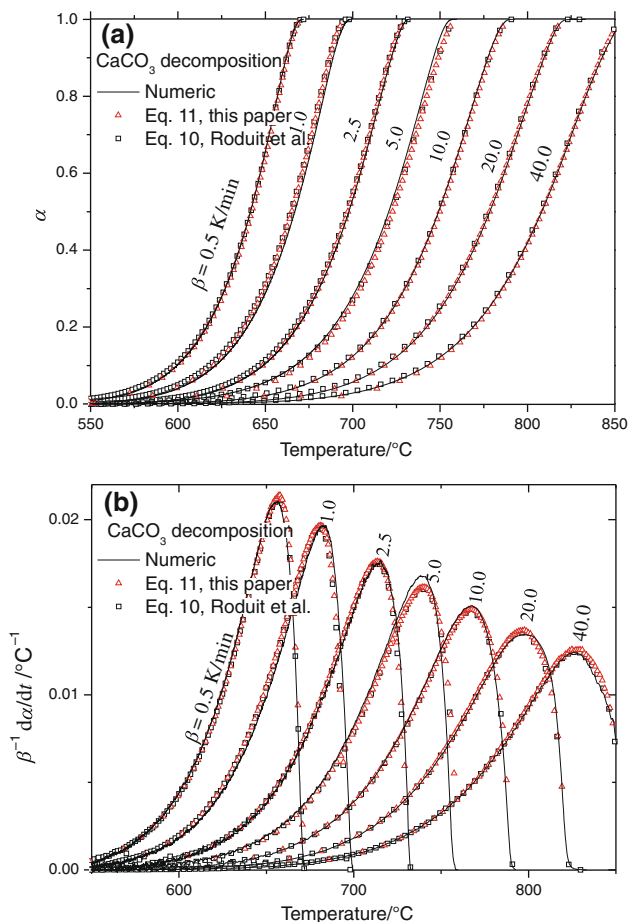

Fig. 6 *Solid line*: Evolution of the transformed fraction for the numerical simulation of the crystallization of amorphous silicon when it is held at a constant temperature of 650 °C. *Symbols*: Isothermal predictions (for the sake of clarity only one out of every 18 points is plotted)

Experimental data: thermal decomposition of CaCO₃

Last but not the least, we will analyze a real case: the thermogravimetric (TG) curves of the thermal decomposition of $CaCO_3$. The experiments were carried out in a Mettler Toledo thermogravimetric analyzer (TGA851LF model). The samples were placed in open alumina crucibles. A flow of 300 mL min^{-1} of high purity nitrogen was kept constant inside the furnace [48]. We performed seven different measurements at heating rates ranging from 0.5 to 40 K min^{-1}.

In Fig. 7, we have plotted the evolution of the transformation rate, which was obtained directly from the first time derivative of the TG signal normalized to the total mass change. To check the reliability of the isoconversional analysis, we have plotted, in Fig. 7, the non-isothermal prediction delivered by Eqs. 9 and 11. There is a good agreement between both the predictions and the actual evolution.
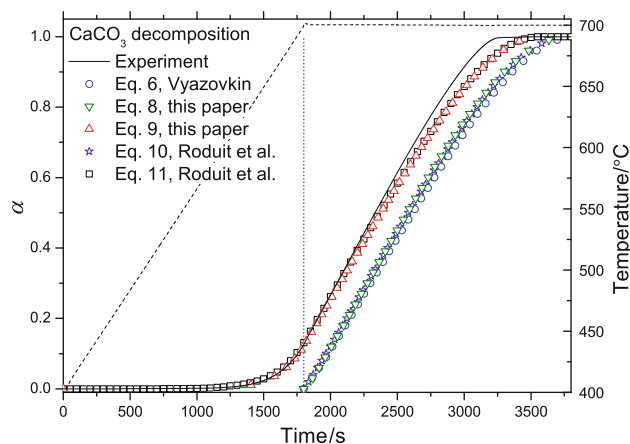
Fig. 8 *Solid line*: Evolution of the transformed fraction for the thermal decomposition of $CaCO_3$ measured by TG when the sample is heated up to 700 °C at 10 K min^{-1} and then is held at 700 °C for 1 h. *Symbols*: Isothermal and non-isothermal predictions (for the sake of clarity only one out of every 50 points is plotted). *Dashed line*: experimental evolution of the sample temperature. *Dotted line*: Onset of the isothermal period

Isothermal measurements are limited by the difficulty of reaching a given temperature while avoiding the partial transformation of the sample. An initial fast heating rate or introducing the sample when the furnace has reached the selected temperature may result in significant instabilities at the beginning of the isothermal measurement, while a slow heating rate may result in a significant initial degree of transformation. At this point, it is better to use a moderate initial heating rate and a non-isothermal prediction to account for the transformation that takes place during the constant heating rate stage. In Fig. 8, we have used a solid line to show the evolution of the transformed fraction for a temperature program that consists of heating the sample from room temperature up to 700 °C at 10 K min^{-1} followed by an isotherm at 700 °C. It is noticed that the thermal instability at the beginning of the isothermal regime is practically negligible, as can be seen by the evolution of the measured temperature (dashed line). Conversely, the evolution predicted by the isothermal methods, Eqs. 6, 8, and 9, exhibits a time shift related to the transformation that takes place during the constant heating rate stage. Furthermore, the non-isothermal methods deliver a significantly more accurate prediction. This means that, in general, the transformation that takes place before the isothermal period is reached and cannot be neglected.

Fig. 7 *Solid line*: Evolution of the transformed fraction (**a**) and the transformation rate (**b**) for the thermal decomposition of $CaCO_3$ measured by TG at several heating rates, β. *Symbols*: Non-isothermal predictions (for the sake of clarity only one out of every 60 to 20 points is plotted depending on the heating rate)

Conclusions

In this study, we have reviewed the most accurate isothermal model-free prediction methods, i.e., those by Vyazovkin

[25] and Roduit et al. [12]. The method of Roduit et al. is exact within the isoconversional hypothesis, while Vyazovkin's method assumes constant activation energy during integration. We have transformed Vyazovkin's method into an exact method by introducing finite differences. In addition, the use of finite differences simplifies the generalization of this method so that it holds under an arbitrary temperature program. Since the method of Roduit et al. is also based on finite differences, its generalization to non-isothermal conditions is straightforward.

Non-isothermal predictions are useful for designing more versatile thermal treatments, for working in more realistic conditions, and for extending the use of isothermal analysis. In addition, non-isothermal predictions provide an easy way to check the goodness of the isoconversional hypothesis: experimental data obtained under a constant heating rate can be compared with the predicted evolution for the same temperature program.

We have stated that the intrinsic inaccuracies of the method of Roduit et al. results in a time shift for those transformations where the transformation rate vanishes at the very first stages under isothermal conditions (sigmoid transformations). However, in many practical situations, this inaccuracy is insignificant, i.e., the method of Roduit et al. delivers virtually the same prediction.

Finally, in the case of complex transformations, the differences between the Vyazovkin's method and the exact methods are minimal. Therefore, when the isoconversional hypothesis is an approximation, the inaccuracy of the Vyazovkin method within the isoconversional hypothesis is practically irrelevant [26].

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