

**Exact analytical solution for the Kissinger equation: determination of the peak temperature and general properties of thermally activated transformations**

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**Abstract**

A key parameter of many transformations when heated at a constant rate is the peak temperature, i.e., the temperature at which the transformation rate is at its maximum. The most universal approach to determining peak temperature for thermally activated transformations is the Kissinger equation. In this paper we solve Kissinger equation to deduce the exact dependence of the peak temperature on the heating rate. This analytical solution is based on the Lambert  $W$ -function. In addition, an approximate solution is derived that is used to infer general properties of thermally activated processes and to obtain a test to check the validity of Kissinger method.

**Keywords:** Kissinger equation, Kinetics, Peak temperature, Non-isothermal, Lambert function, thermally activated transformation, constant heating rate.

## 1. Introduction

In thermally activated and homogeneous transformations the rate of change of a substance can be described as a function of the temperature and its state, and that the system state is a function of a single parameter: the degree of transformation,  $\alpha$  ( $0 < \alpha < 1$ ). Under this assumption, and supposing that the transformation is ruled by a single mechanism, the transformation rate is described by a differential equation where the contribution of the temperature and  $\alpha$  may be factorized [1,2]:

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

where  $t$  is time,  $T$  is the temperature,  $k(T)$  is the rate constant and  $f(\alpha)$  is the conversion function for the particular transformation mechanism. Besides, in many thermally activated solid state transformations  $k(T)$  is described by the Arrhenius dependence [3–6]:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where  $A$  is the pre-exponential term,  $E$  is the activation energy and  $R$  is the universal gas constant. When the temperature is raised at a constant rate,  $\beta \equiv dT/dt$ , Eq. 1 still holds provided that the transformation rate does not depend on the thermal history. Thus, under continuous heating conditions, the explicit dependence on time of Eq. 1 can be eliminated:

$$\frac{d\alpha}{dT} = \frac{1}{\beta} k(T) \cdot f(\alpha). \quad (3)$$

From Eq. 3 one can easily derive the *Kissinger equation* [7] (see appendix A) that relates the peak temperature,  $T_M$ , with the kinetic parameters and heating rate:

$$\ln\left(\frac{\beta}{T_M^2}\right) = -\frac{E}{RT_M} + \ln\left(-\frac{AR}{E} f'(\alpha_M)\right) \quad (4)$$

where  $f'(\alpha_M) \equiv df/d\alpha|_{\alpha=\alpha_M}$  and  $\alpha_M$  is the degree of transformation at  $T_M$ .

Eq. 4 has been used to determine the activation energy for a large variety of transformations [8–15]. Kissinger method relies on the determination of the peak temperature  $T_{M,i}$  from experiments carried at different heating rates  $\beta_i$ . The activation energy is obtained from a linear fit of the plot  $\ln(\beta_i/T_{M,i}^2)$  versus  $1/T_{M,i}$ . Although Eq. 4

is exact, the Kissinger method is approximate because it assumes that the second term of the right hand side does not depend on the heating rate,  $\beta$ . Kissinger originally derived his equation for a first-order reaction, in this case  $f'(\alpha_M) = -1$  and its kinetic method is exact. For most kinetic models  $f'(\alpha_M)$  is approximately constant provided that  $E/RT_M$  is large enough [15–20] (see appendix A). In Refs. [16–18,21,22] the values of  $\alpha_M$  and  $f'(\alpha_M)$  are given, and for many reaction models  $f'(\alpha_M) \approx -1$ . For most kinetic models the percent error in the calculation of the activation energy is below 2% if  $E/RT_M > 10$  [23] (a review of the literature reveals that, for most transformations,  $E/RT_M > 10$  [24]). Typically the activation energy is around 1.5 eV (145 kJ/mol); thus, for peak temperatures around 600 K,  $E/RT_M \sim 30$ , and for  $T_M \sim 1700$  K,  $E/RT_M \sim 10$ . For smaller values of  $E/RT_M$  other temperature dependencies may emerge due to the weak thermal activation and, therefore, Eqs. 1-4 must be applied with caution.

The Kissinger method has received more than four thousand citations [25]. The reason for this success are the simplicity of the model, its relative independence of the reaction mechanism [23,26] and its robustness. This is because the strong temperature dependence of the rate constant ensures a reliable determination of the activation energy from Eq. 4. The validity of Eq. 4, and therefore that of Kissinger method, is not limited by its accuracy but rather to the ability of Eq. 1-3 to describe the actual kinetics. Recent papers [10,26–28] reveal that the Kissinger method is erroneously applied to systems that are not governed by Eqs. 1-3. The log scale involved in the Kissinger plot smoothes out the kinetic data. Consequently, linear plots are obtained even though Eqs. 1-3 do not describe the actual kinetics. Thus, validity of Kissinger method cannot be judged from the goodness of the linear fit. [29].

The Kissinger method fails when multiple mechanisms are involved [31–34], for heterogeneous systems [35], for transformations where the activation energy depends on  $\alpha$  (such as structural relaxation [27,36,37]) or for transformations depending on parameters other than  $\alpha$  and  $T$  (such as solid-gas reactions that depend on the local gas pressure [10,16,38]). To deal with these complex systems isoconversional methods have

been developed that, in addition and within the framework of the isoconversional hypothesis [39], are exact or significantly more accurate [10,11,40–43]

In general, the Kissinger method also fails for heterogeneous systems. However, in some relevant cases such as crystallization of amorphous materials, Eqs. 1-3 approximately hold and it provides a reliable determination of the activation energy [8,28,44]. Since the Kissinger method assumes a constant temperature rise it cannot be directly applied to constant cooling measurements [26,45]. Similarly, some thermally activated processes such as glass crystallization or melt crystallization do not follow an Arrhenius behavior. In these circumstances the method may be modified [21,26,46]. In particular, it has been numerically shown that it provides reliable results [21] for a Vogel-Fulcher temperature dependence [47] but it fails in the case of melt crystallization [21,28]. Finally, thermal gradients, related to heat propagation through the sample [48,49] or to the heat evolved from the sample [50,51], pose difficulties to the correct determination of the peak temperature.

As far as we know, no exact analytical solution of Eq. 4 for the peak temperature has been published. Knowledge of the peak temperature is important for both experimental and theoretical purposes. Besides having an accurate solution, it is also useful in reducing the computation time required for numerical simulations. In this paper we solve Eq. 4 and we provide analytical solutions with sufficient accuracy for experimental, theoretical and numerical purposes. Finally, the analytical solution is used to disclose some general properties of thermally activated processes and to develop a test to check the validity of the Kissinger method.

## 2. Peak temperature: solution of the Kissinger equation

Eq. 4 can be expressed in terms of the reduced activation energy  $x_M \equiv E / RT_M$ ,

$$4z^2 = x_M^2 e^{x_M}, \quad (5)$$

where  $z$  contains all the system parameters:

$$z \equiv \frac{1}{2} \sqrt{-\frac{EAf'(\alpha_M)}{R\beta}} \quad (6)$$

Our goal is to determine  $x_M$  as a function of  $z$ :  $x_M(z)$ . If we take the square root of both sides of Eq. 5 we obtain,

$$z = W(z)e^{W(z)} \quad (7)$$

where  $W \equiv \frac{1}{2}x_M$ . Eq. 7 turns out to be the definition of the transcendental Lambert  $W$ -function [52]. Lambert  $W$ -function has two branches: the principal one,  $W_0$ , which corresponds to  $W(z)>0$ , and the negative branch  $W_{-1}$ . The solution of the Kissinger equation is restricted to  $W_0$  because  $x_M \equiv E/RT_M > 0$ .  $W_0$  is a single-valued function that monotonically increases with  $z$ . Thus the peak temperature is given by

$$\frac{E}{RT_M} = x_M = 2W_0(z) = 2W_0\left(\frac{1}{2}\sqrt{-\frac{EAf'(\alpha_M)}{R\beta}}\right). \quad (8)$$

It is worth recalling that Eq. 8 is exact, no approximation has been used so far.

## 2.1 Analytical solution for experimental and theoretical purposes

There are several approximations to the Lambert  $W$ -function [53,54]. As we discussed in the introduction,  $x_M > 10$  and typically  $x_M$  is around 20 or 30; the related  $z$  values are 742,  $2.2 \times 10^5$  and  $4.9 \times 10^7$ . Thus, we are interested in an asymptotic expansion for large values of  $z$ . In particular, the solution  $W_0 = \ln(z/\ln(z/\dots))$  can be used to obtain a sequence of approximate analytical solutions [53,54],

$$W_0^{n+1} = \ln\left(\frac{z}{W_0^n}\right), \quad W_0^0 = \ln(z) \quad (9)$$

For  $x_M > 10$  ( $z > 742$ ), the maximum relative errors of  $W_0^1$  and  $W_0^2$  are 5.6% and 2.1%, respectively. This error is reduced to 1.1% and 0.21% respectively for  $x_M > 20$ . In Ref. [24] the first term of this sequence is also proposed as a solution that takes as an initial term a value of  $x_M$  inside the interval of interest.

In Fig. 1 we have plotted the exact solution, Eq. 8, for a parameter range that corresponds to  $10 < x_M < 40$ . The nearly linear relationship between  $x_M$  and  $\ln(z)$  is noteworthy. To take advantage of this property, we have approximated the exact solution by its first order series expansion in  $\ln(z)$  around a reference peak temperature  $T_{M,0}$  related to a heating rate  $\beta_0$  (see appendix B),

$$x_M = x_0 + \frac{x_0}{2 + x_0} \ln \frac{\beta_0}{\beta}. \quad (10)$$

where  $x_0 \equiv E/RT_{M,0}$ . From the second term of the series expansion, we can evaluate the relative percent error of the approximate solution, Eq. 10, (see appendix B),

$$e\% = \frac{1}{(2 + x_0)^3} \left( \ln \frac{\beta_0}{\beta} \right)^2 \times 100 \quad (11)$$

For instance, if we assume that  $\beta$  spans 3 decades (say from 0.1 to 100 K/min) and  $\beta_0$  is a central value (say 3 K/min), then  $(\ln \beta_0 / \beta)^2 \approx 12$  and the percent relative error for  $x_M=20$  is around 0.1%. In the inset of Fig. 1 we have plotted  $e\%$  as a function of  $x_M$  assuming that  $\beta$  spans 3 decades. One can state that the inaccuracies of Eq. 10 are well below 1%, i.e., they are irrelevant in practical situations provided that  $x_M > 10$ .

The reader may think that Eq. 10 is not really a solution of the Kissinger equation delivering  $x_M$  (or  $T_M$ ) as a function of the system parameters,  $E$ ,  $A$ ,  $\beta$  and  $f(\alpha_M)$ , for two reasons: a) these parameters do not appear explicitly and b) Eq. 10 can only be applied if a particular solution  $(\beta_0, x_0)$  is already known. However, a particular solution can be directly obtained by introducing  $x_0$  into the Kissinger Eq. 5,  $4z_0^2 = x_0^2 e^{x_0}$ , and solving Eq. 6 to obtain  $\beta_0$ . Thus, we can express Eq. 10 as a function of  $z$ ,

$$x_M = x_0 + \frac{2x_0}{2 + x_0} \ln \frac{z}{z_0}. \quad (12)$$

In Fig 1 we have plotted Eq. 12 with  $x_0=20$  together with the exact solution for  $10 < x_M < 40$ . One can verify that Eq. 12, and therefore Eq. 10, provide a quite accurate solution even for  $x_M$  values significantly different than  $x_0$ . Hence, the choice of the reference value is not critical at all. Besides and as we will see in Section 3, a solution in terms of  $\beta$ , Eq. 10, is more useful to understand several general properties of thermally activated processes.

## 2.2 Analytical solution for numerical purposes

In this section we are looking for an analytical solution with accuracy of the order of double-precision floating-point numbers, i.e., accuracy of the order of  $10^{-16}$  or better. For  $x_M > 10$ , the solution  $W_0^n$  achieve this accuracy for  $n=22$ . Taking into account that in general  $x_M > 20$ ,  $n=16$  suffices to achieve this accuracy.

A less time-consuming computing-time alternative consists of replacing the solution  $W_0 = \ln(z/\ln(z/\dots))$  by its doubly-infinite expansion [53]:

$$\begin{aligned}
W_0 = L_0 - L_1 + \sum_{k=0} \sum_{m=1} (-1)^k c_{k,m} \frac{L_1^m}{L_0^{m+k}} = & L_0 - L_1 + \frac{L_1}{L_0} + L_1 \frac{(-2 + L_1)}{2L_0^2} + L_1 \frac{(6 - 9L_1 + 2L_1^2)}{6L_0^3} + \\
& + L_1 \frac{(-12 + 36L_1 - 22L_1^2 + 3L_1^3)}{12L_0^4} + L_1 \frac{(60 - 300L_1 + 350L_1^2 - 125L_1^3 + 12L_1^4)}{60L_0^5} + \dots
\end{aligned}
\tag{13}$$

where  $L_0 = \ln(z)$ ,  $L_1 = \ln(L_0)$  and  $c_{k,m}$  is a positive Stirling number of the first kind. For instance, for  $m+k=16$  the accuracy is  $4.5 \times 10^{-13}$  and  $1.1 \times 10^{-16}$  for  $x_M > 10$  and  $x_M > 20$ , respectively.

### 3. Properties of thermally activated processes

In this section we will apply the analytical solutions derived above to infer some properties of thermally activated processes. In particular, we analyze the dependence of the peak temperature, peak width and signal intensity on the heating rate.

#### 3.1 Dependence of the peak temperature on the heating rate

The dependence of the peak temperature on the heating rate may be directly derived from the approximate solution Eq. 10:

$$\frac{1}{T_M} = -\frac{x_0}{2+x_0} \frac{R}{E} \ln \beta + \left( \frac{1}{T_{M,0}} + \frac{x_0}{2+x_0} \frac{R}{E} \ln \beta_0 \right) \tag{14}$$

Therefore a plot of  $1/T_M$  versus  $\ln \beta$  must deliver a straight line. We have checked the latter prediction against the experimental and theoretical curves of the thermal decomposition of  $\text{CaCO}_3$  (see Fig. 2). The experimental details are given in ref. [30]. According to ref. [30], the decomposition of  $\text{CaCO}_3$  is approximately described by

a  $n$ -reaction model,  $f(\alpha) = (1 - \alpha)^n$ , with  $n=0.42$ ,  $E=195$  kJ/mol and  $\ln A=7.14$  ( $A$  in  $s^{-1}$ ). In Fig 3 we have plotted  $1/T_M$  versus  $\ln\beta$  for the experimental and theoretical curves shown in Fig. 2 together with the predicted dependence of Eq. 14 taking as reference  $\beta_0=10$  K/min and  $T_{M,0}=1032$  K ( $x_0=22.73$ ). The agreement between numerical and experimental data with Eq. 14 is remarkable. Note, that the straight line in Fig. 3 is not a linear fit but the predicted dependence according to Eq. 14 and using the kinetic parameters derived from the Kissinger method (the details of the kinetic analysis are given in Ref. [30]).

From Eq. 14 one can disclose some general trends of the thermally activated reactions. For instance, one can verify that the peak temperature increases with the heating rate. As for the separation between two peaks  $T_{M,0}$  and  $T_{M,1}$  performed at two different heating rates,  $\beta_0$  and  $\beta_1$  respectively,

$$\frac{T_{M,1} - T_{M,0}}{T_{M,0}^2} \approx \frac{1}{T_{M,0}} - \frac{1}{T_{M,1}} = \frac{x_0}{2 + x_0} \frac{R}{E} \ln \frac{\beta_1}{\beta_0} \quad (15)$$

Hence, the peak separation scales as the logarithm of the heating rate. Thus, for a non-isothermal kinetic analysis, the heating rates should be equally distributed in a logarithmic scale. In addition, the peak separation is proportional to the reciprocal of the activation energy, therefore for processes that take place at the same temperature range, the larger the activation energy, the smaller the temperature separation.

Finally the logarithm in the right hand side of Eq. 15 significantly limits the temperature range that can be explored with non-isothermal experiments. For instance, according to Eq. 15 and for a process that takes place at 600 K with typical activation energy around 145 kJ/mol, the temperature range that can be explore varying 3 decades the heating rate is only 145 K. In Fig. 2 the separation between the peaks obtained at 0.5 and 80 K/min is 200 K and the separation predicted from Eq. 15 is 211 K (with  $E=195$  kJ/mol and  $T_{M,0}=1032$  K).

### 3.2 Dependence of the peak width on the heating rate

The width at half maximum,  $\Delta t$ , of the transformation rate peak is given by [21,30],



$$\ln \Delta t = \frac{E}{RT_M} + \ln\left(\frac{\Delta t'}{A}\right) \quad (16)$$

where  $\Delta t'$  is a constant that depends on the reaction model. If we substitute the approximate solution, Eq. 10, into the previous relationship we obtain,

$$\ln \Delta t = -\frac{x_0}{2+x_0} \ln\left(\frac{\beta}{\beta_0}\right) + \ln(\Delta t_0) \quad (17)$$

where  $\ln \Delta t_0 = x_0 + \ln(\Delta t'/A)$  is the width of the peak when the heating rate is  $\beta_0$ .

As a result, a plot of  $\ln \Delta t$  versus  $\ln \beta$  must deliver a straight line. We have checked the latter prediction against the experimental data obtained from the crystallization of amorphous silicon, a-Si, (see Fig. 4). The experimental details are given in ref. [30]. According to ref. [30], crystallization of a-Si is approximately described by a KJMA model [8,55–59],  $f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{\frac{n-1}{n}}$ , with  $n=4$ ,  $E=346$  kJ/mol,  $\ln A=37.5$  (A in s<sup>-1</sup>),  $f'(\alpha_M) = -1$  and  $\Delta t' = 2.44639/4$ . In Fig 5 we have plotted  $\ln \Delta t$  versus  $\ln \beta$  for the experimental evolutions shown in Fig. 4 together with the predicted dependence of Eq. 17. The agreement between the experimental data with the predicted dependence, Eq. 17, is remarkable. Note again, that the solid line is not a linear fit but the prediction obtained from Eq. 17 using the activation energy delivered by the Kissinger method and the measured peak width for  $\beta_0=1$  K/min.

Since  $\Delta T = \beta \Delta t$ , the peak width in temperature scale is,

$$\ln \Delta T = \frac{2}{2+x_0} \ln\left(\frac{\beta}{\beta_0}\right) + \ln(\Delta T_0) \quad (18)$$

Note, that the term  $2/(2+x_0)$  goes to zero when  $x_0 \rightarrow \infty$ . Since  $x_0 > 10$ , typically above 20,  $\Delta T$  is roughly constant when compared to the evolution of  $\Delta t$  with  $\beta$ . Moreover, the term  $x_0/(2+x_0)$  tends to one when  $x_0 \rightarrow \infty$ . Therefore, the peak width in time is roughly proportional to the reciprocal of the heating rate. For instance, in Fig 2 the peak width ranges from 42 to 87 K and from 5090 to 60 s when  $\beta$  varies from 0.5 to 80 K/min. That is, when the heating rate is raised from 0.5 to 80 K/min the peak width in temperature increases by a factor 2 while the peak width in time decreases by a factor 85.

### 3.3 Dependence of the signal intensity on the heating rate

In several thermal analysis techniques such as DSC or DTA the signal intensity is proportional to the transformation rate, so through the analysis of the transformation rate at the peak temperature,  $d\alpha/dt|_{T_M}$ , we will be able to analyze the dependence of the signal intensity on the heating rate. This dependence can be disclosed by substituting the approximate solution, Eq. 10, into Eqs. 1-2:

$$\ln \frac{d\alpha}{dt} \Big|_{T_M} = \frac{x_0}{2+x_0} \ln \left( \frac{\beta}{\beta_0} \right) + \ln \frac{d\alpha}{dt} \Big|_{T_{M,0}} \quad (19)$$

Therefore, the signal intensity increases with  $\beta$ . Since the area under the peak is constant and equal to 1; the peak height must be proportional to  $1/\Delta t$ . This relationship is obtained from the combination of Eqs. 17 and 19,

$$d\alpha/dt|_{T_M} \times \Delta t = \Delta t' f(\alpha_M) \quad (20)$$

This constant on the right hand side of Eq. 20 depends solely on the reaction model.

In the previous section we have seen that the peak width roughly scales as  $1/\beta$ ; so, the signal intensity must be roughly proportional to  $\beta$ . The latter conclusion is also apparent from Eq. 19 since the term  $x_0/(2+x_0)$  tends to one when  $x_0 \rightarrow \infty$ . In kinetic studies it is important to explore a relatively large range of heating rates. As a result, the time and the peak height scales may differ significantly from one experiment to another. Therefore, a plot of all the curves recorded at different heating rates is not convenient. However, it is possible to rescale time and transformation rate to achieve a plot where all the peaks have a similar size. This has been done in Figs. 2 and 4. Note that in Figs. 2 and 4 the transformation rate has been divided by  $\beta$  while the time scale has been multiplied by  $\beta$  (it has been converted into temperature).

### 3.4 A criterion to test the validity of Kissinger method

Kissinger method relies exclusively on the determination of the peak temperature, so useful information such as the peak shape is neglected. The combination of different mechanisms or artifacts related to temperature gradients may have a significant effect on the peak width. Thus, the peak width provides useful information to check the validity of Eq. 1 to describe the actual kinetics. From Eq. 17, the plot of  $\ln\Delta t$  versus  $\ln\beta$  must deliver a straight line where the value of the slope can be determined from the Kissinger analysis.

For instance, we have simulated two equally weighted  $n$ -order reactions:

$$\frac{d\alpha_1}{dt} = A_1 \exp\left[-\frac{E_1}{RT}\right](1-\alpha_1), \quad \frac{d\alpha_2}{dt} = A_2 \exp\left[-\frac{E_2}{RT}\right](1-\alpha_2)^2 \quad \text{and} \quad \alpha = \frac{1}{2}(\alpha_1 + \alpha_2), \quad (21)$$

where  $E_1=80 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $A_1=1.17\times 10^8 \text{ s}^{-1}$ ,  $E_2=120 \text{ kJ}\cdot\text{mol}^{-1}$  and  $A_2=1.67\times 10^{84} \text{ s}^{-1}$ . In Fig. 6 we have plotted the simulated evolutions and in Fig. 7 we have plotted the Kissinger analysis. The parameters for the numerical simulation have been chosen so that the complex nature of the kinetics it is not apparent from the shape of the peaks; no double peak is observed and the only significant feature is a shoulder for  $\beta=0.5 \text{ K/min}$ . Despite the fact that we are analyzing a complex transformation, the points of the Kissinger plot are nicely aligned. The activation energy determined from the slope of the linear fit is  $86.1 \text{ kJ}\cdot\text{mol}^{-1}$ . The plot of  $\ln\Delta t$  versus  $\ln\beta$  also delivers a straight line, but the slope determined from the linear fit does not coincide with the expected value according to Eq. 17. The linear fit delivers a slope of  $-1.03$  while according to Eq. 17 its absolute value,  $x_0/(2+x_0)$ , is always smaller than 1. Taking as reference  $\beta_0=5 \text{ K/min}$ , the slope predicted by Eq 17 is 0.93 which is significantly smaller than the one delivered by the linear fit. In Fig. 7 we have also plotted the solution delivered by Eq. 16, and clearly it deviates from the observed behavior.

Due to heat evolved from the sample, the thermal decomposition of yttrium trifluoroacetate undergoes a thermal runaway and the peak shape is significantly altered [51]. In Fig. 8 we have plotted the evolution of the decomposition of yttrium trifluoroacetate to form yttrium fluoride (the experimental details are given in ref. [60]). Fig. 9 shows the Kissinger and the  $\ln\Delta t$  versus  $\ln\beta$  plots. In both cases, the data are well aligned. The activation energy delivered by the Kissinger method is  $165 \text{ kJ}\cdot\text{mol}^{-1}$ . Taking as reference  $\beta_0=5 \text{ K/min}$ , the expected slope for the  $\ln\Delta t$  versus  $\ln\beta$  plot is

-0.94, the magnitude of which is significantly smaller than the value delivered by the linear fit, -1.27. In addition, a slope of absolute value above 1 is in contradiction with the prediction of Eq. 17 and evidences that the actual kinetics cannot be described by Eq. 1.

## **Conclusions**

We have derived the exact relationship of the peak temperature for thermally activated processes in terms of the transcendental Lambert  $W$ -function. In addition, we have derived an approximate analytical solution for experimental and theoretical purposes.

We have shown that in non-isothermal kinetic studies and for processes that take place at the same temperature range, the separation between peaks obtained at different heating rates increases steadily when the activation energy diminishes. We have also shown that in non-isothermal analysis, the different heating rates should be equidistant in a logarithm scale. In addition, the temperature range analyzed by non-isothermal measurements is relatively narrow, typically few hundreds of Kelvin when the heating rate is varied over three decades.

We have shown that the duration of a process, peak width, is roughly proportional to the reciprocal of the heating rate but the peak width in the temperature scale is nearly constant when compared to the time peak width. As for the signal intensity, it is approximately proportional to the heating rate.

Finally, we have introduced a test to check whether a transformation is ruled by a single-step kinetics. This test is based on the linear relationship between the logarithm of the heating rate and the logarithm of the peak width.

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## **Appendix A. Derivation of the Kissinger equation**

The peak temperature,  $T_M$ , i.e., the temperature at which the transformation rate is at its maximum is obtained by imposing that the first derivative of the transformation rate, Eqs 1-2, is zero,

$$\frac{d^2\alpha}{dt^2} = \left( \frac{d\alpha}{dt} \left[ \frac{df(\alpha)}{d\alpha} k(T) + \beta \frac{E}{RT^2} \right] \right)_{T=T_M} = 0 \quad (\text{A.1})$$

Since at the maximum the heating rate is non zero,

$$\frac{\beta}{T_M^2} = -\frac{R}{E} f'(\alpha_M) A e^{-\frac{E}{RT_M}} \quad (\text{A.2})$$

where  $\alpha_M$  is the degree of transformation when  $T=T_M$ . Finally, taking logarithms at both sides we obtain,

$$\ln\left(\frac{\beta}{T_M^2}\right) = -\frac{E}{RT_M} + \ln\left(-\frac{AR}{E} f'(\alpha_M)\right) \quad (\text{A.3})$$

Kissinger method is based on the determination of the peak temperature  $T_{M,i}$  for non-isothermal experiments performed at different heating rates  $\beta_i$ . The activation energy is determined from the slope of the plot of  $\ln(\beta_i/T_{M,i}^2)$  versus  $1/T_{M,i}$ . Therefore, Kissinger method assumes that the term  $f'(\alpha_M)$  is constant, i.e., independent of  $\beta$  or  $T_M$ . Kissinger initially derived its method for a first order reaction ( $f(\alpha)=1-\alpha$ ). In this case  $f'(\alpha)=1$  and the method is exact. The validity of the method may be extended to other kinetics by integrating Eq. 1:

$$g(\alpha) \equiv \int_0^\alpha \frac{du}{f(u)} = \frac{EA}{\beta R} P\left(\frac{E}{RT_\alpha}\right) \quad (\text{A.4})$$

where  $p(x) \equiv \int_x^\infty \frac{\exp(-u)}{u^2} du$  is the temperature integral [61] and  $T_\alpha$  is the temperature at which a degree of transformation  $\alpha$  is attained. Combining Eqs. A.2 and A.4 we obtain,

$$f'(\alpha_M) g(\alpha_M) = -h\left(\frac{E}{RT_M}\right) \quad (\text{A.5})$$

where  $h(x) \equiv p(x)x^2e^x$ . The temperature integral can be developed by an alternate series expansion [62],

$$p(x) = \frac{\exp(-x)}{x^2} \sum_{i=0}^{\infty} (-1)^i \frac{(i+1)!}{x^i} \quad (\text{A.6})$$

For large values of  $x$ ,  $p(x)$  may be approximate by the first term of the series. This is the well known Murray's approximation [63]. Under this approximation,

$$f'(\alpha_M)g(\alpha_M) \approx 1 \quad (\text{A.7})$$

Therefore, for large values of  $E/RT_M$ ,  $\alpha_M$  is a constant that depends on the reaction model but it is independent of  $\beta$  and  $T_M$  [17,18]. From Eq. A.5 it is clear that the accuracy of the Kissinger method is related to the reaction model and the value of  $E/RT_M$ . However, it has been show that the accuracy is mainly related to  $E/RT_M$  [20,23,26], therefore Kissinger method is relatively independent of the reaction model.

## Appendix B. Taylor series of $2W_0$

The Taylor order series expansion of Eq. 8 in  $\ln(z)$  around a reference peak temperature  $T_{M,0}$  which is related to a heating rate  $\beta_0$  is given by,

$$x_M = x_0 + 2 \left. \frac{dW}{d \ln z} \right|_{z=z_0} \times (\ln z - \ln z_0) + 2 \frac{1}{2!} \left. \frac{d^2W}{d \ln z^2} \right|_{z=z_0} \times (\ln z - \ln z_0)^2 + \dots \quad (\text{B.1})$$

where  $x_0 \equiv E/RT_{M,0}$  and  $z_0 = \frac{1}{2} \sqrt{-\frac{EAf'(\alpha_M)}{R\beta_0}}$ . Taking into account that

$\frac{dW}{dz} = \frac{1}{z} \frac{W}{1+W}$  and that  $(\ln z - \ln z_0) = \frac{1}{2} \ln(\beta_0 / \beta)$ , Eq. (B1) becomes,

$$x_M = x_0 + \frac{x_0}{2+x_0} \ln \frac{\beta_0}{\beta} + \frac{x_0}{(2+x_0)^3} \left( \ln \frac{\beta_0}{\beta} \right)^2 + \dots \quad (\text{B.2})$$

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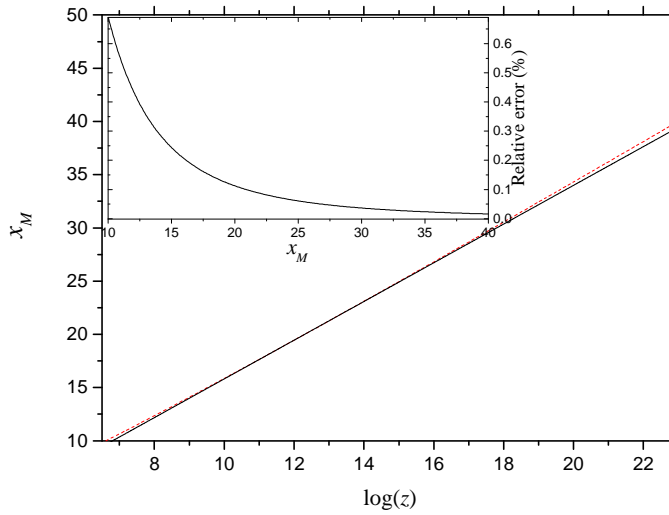
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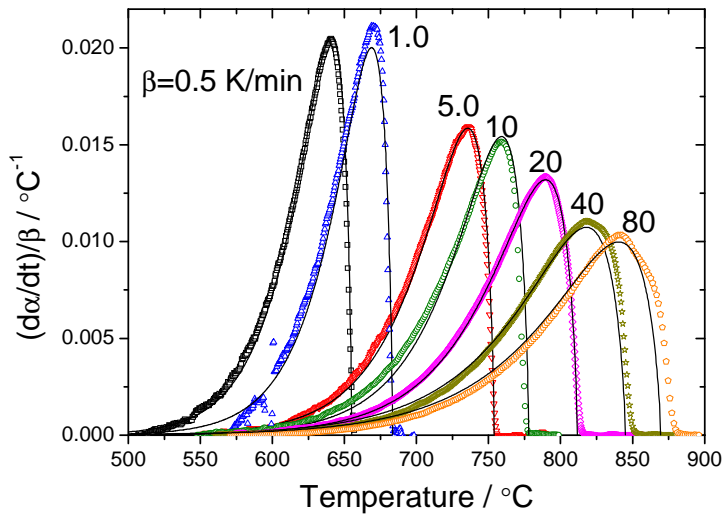
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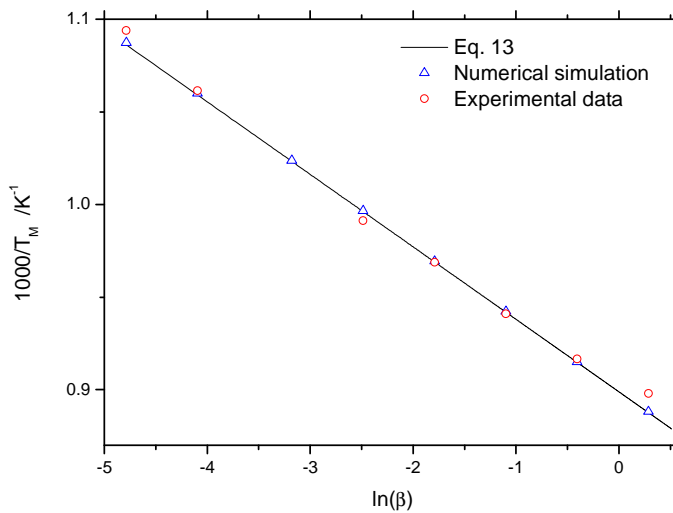
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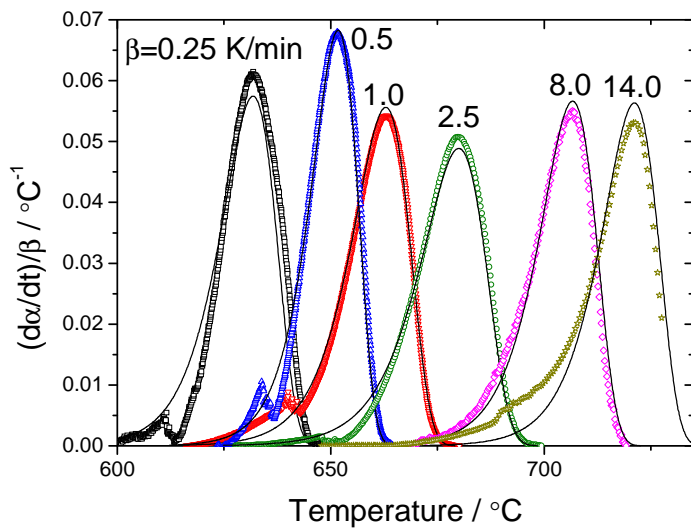
**Figure 1.** Solid line: plot of the exact solution, Eq. 8. Dashed line: plot of the approximate solution, Eq. 12, with  $x_0=20$ . Inset: maximum relative error of the first order of Taylor series, Eq. 11, when the heating rate spans along 3 decades.



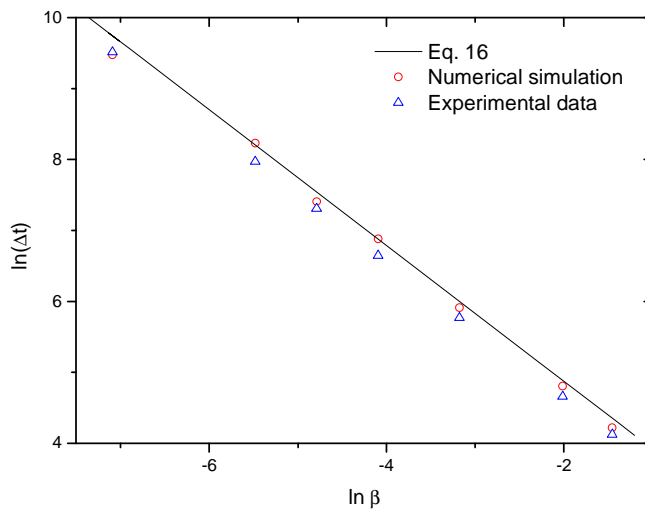
**Figure 2.** Symbols are the measured evolution of the decomposition rate of  $\text{CaCO}_3$  and solid lines are the simulated curves;  $n$ -reaction model with  $n=0.42$ ,  $E=195$  kJ/mol and  $\ln A=7.14$  ( $A$  in  $\text{s}^{-1}$ ).



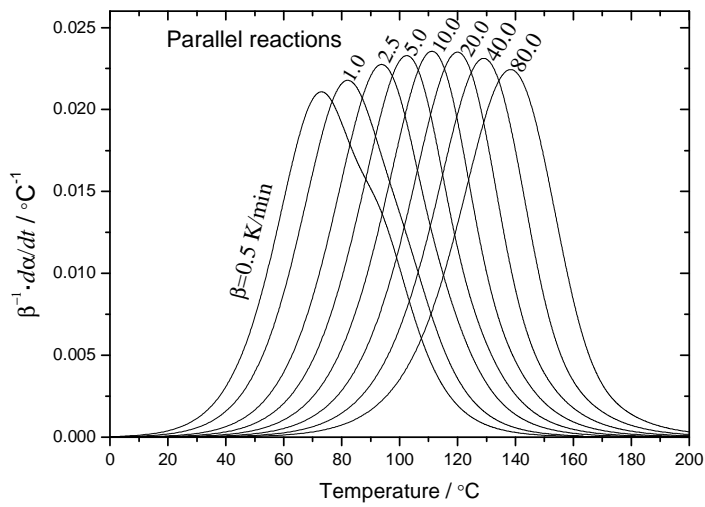
**Figure 3.** Symbols correspond to the experimental and simulated evolutions of the decomposition of  $\text{CaCO}_3$  shown in Fig 2. The solid line is the predicted dependence from Eq. 14 with  $E=195$  kJ/mol,  $\beta_0=10$  K/min and  $T_{M,0}=1032$  K.



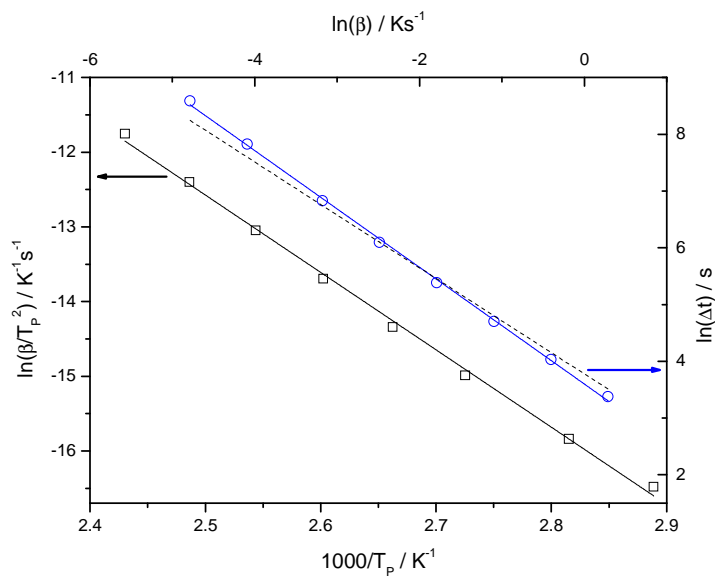
**Figure 4.** Symbols are the measured evolution of the crystallization rate of a-Si and solid lines are the simulated curves; KJMA model with  $n=4$ ,  $E=347$  kJ/mol and  $\ln A=37.5$  ( $A$  in  $s^{-1}$ ).



**Figure 5.** Symbols correspond to the experimental and simulated evolutions of the crystallization of a-Si shown in Fig 4. The solid line is the predicted dependence from Eq. 17 with  $E=346$  kJ/mol,  $\beta_0=10$  K/min,  $T_{M,0}=1032$  K and  $\Delta t_0=973$  s.

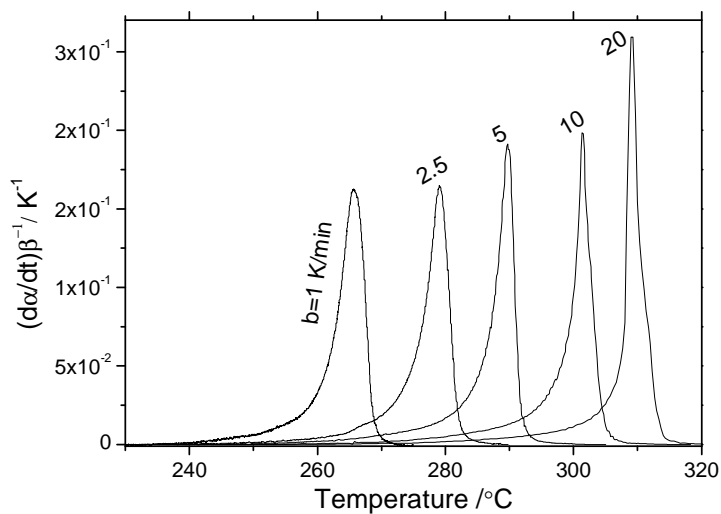


**Figure 6.** Evolution of the transformed fraction for the numerical simulation of two parallel reactions.

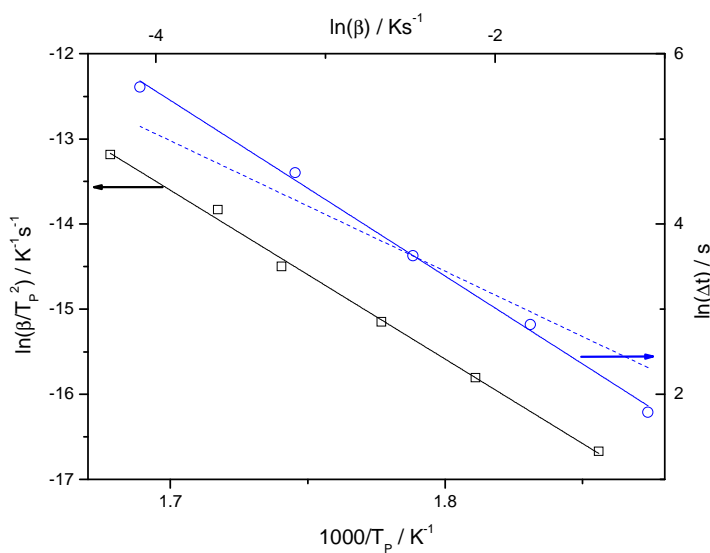


**Figure 7.** Kissinger and  $\ln(\Delta t)$  versus  $\ln(\beta)$  plots for the evolutions shown in Fig. 6. Solid lines are linear fits while the dashed line is the predicted dependence according to Eq. 17.





**Figure 8.** Experimental evolution of the thermal degradation of yttrium trifluoroacetate in the form of powders obtained from TG experiments performed at different heating rates.



**Figure 9.** Kissinger and  $\ln(\Delta t)$  versus  $\ln(\beta)$  plots for the evolutions shown in Fig. 8. The solid lines are linear fits while the dashed line is the predicted dependence according to Eq. 16.