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► **To cite this version:**

Nicolas Sbirrazzuoli. Determination of pre-exponential factor and reaction mechanism in a model-free way. *Thermochimica Acta*, 2020, 691, pp.178707 -. <10.1016/j.tca.2020.178707>. <hal-03491154>

HAL Id: hal-03491154

<https://hal.science/hal-03491154v1>

Submitted on 22 Aug 2022

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Determination of pre-exponential factor and reaction mechanism in a model-free way

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Abstract

Four methods to compute the pre-exponential factor and the mathematical function that describe the reaction mechanism in a model-free way are proposed and their accuracies were estimated using a complex (multi-step) reaction mechanism that has been simulated. It is shown that the use of the compensation effect in association with Friedman's or Vyazovkin's isoconversional methods gives accurate results. Model-free estimation of these parameters can be an efficient tool for the elucidation of complex reaction mechanisms, in complementarity to the estimation of the effective activation energy dependency with temperature and extent of conversion.

Keywords: Isoconversional kinetic analysis; Model-free kinetics; Pre-exponential factor; reaction mechanism; nonisothermal kinetics.

1. Introduction

Isoconversional methods are amongst the more reliable kinetic methods for the treatment of thermoanalytical data, see, for example [1,2,3,4]. They have the advantage of allowing the calculation of the effective activation energy, named E_α , without assuming any particular form of the reaction model, $f(\alpha)$ or $g(\alpha)$, i.e. in a "model-free" way. This is very interesting to obtain information on the reaction mechanism that we want to elucidate. A change in the E_α variation, called the E_α -dependency, can generally be associated with a change in the reaction mechanism or in the rate-limiting step of the overall reaction rate, as measured with thermoanalytical techniques. Most often, only E_α is calculated because to calculate the pre-exponential factor A_α or the mathematical function that describe the reaction mechanism $f(\alpha)$ or $g(\alpha)$ it is necessary to introduce a hypothesis on this mechanism in the equations. Thus, the resulting values are not model-free. However, in some cases it is very useful to know both E_α and A_α . Several examples where a chemical reaction occurred at lower temperature despite a

higher value of E_α were explained by a higher value of A_α [5,6]. Interestingly, the effect may appear in A_α only, when E_α remains unchanged. This was noticed for effect of inert gas pressure on reversible solid-state decomposition [7]. The knowledge of $f(\alpha)$ is also very important for the elucidation of reaction mechanisms. The only method which allows the value of A_α to be determined in a model-free way is the method based on the so-called “compensation effect” (CE). The principle of this method is not straightforward because it uses a fit of the data to finally obtain model-free values of A_α . The validity of the method could be easily checked for a single-step reaction, using simulated data, because a single value of E and A is obtained in this case. Therefore, only one pioneering study reports the validity of the method for multi-step reactions [8]. Indeed, the theoretical A_α -dependency is not known in this case. Thus, the aim of this study is to use a simulated multi-step reaction for which the theoretical A_α -dependency can be determined, to check the accuracy of four methods to evaluate A_α and $f(\alpha)$ in a model-free way, and to determine the most accurate methods. The work is a completion of a previously published article [9].

2. Theoretical part

2.1. Kinetic methods

The general form of the basic rate equation is usually written as [1]:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

where T is the temperature, $f(\alpha)$ is the differential form of the mathematical function that describe the reaction model that represents the reaction mechanism, E is the activation energy, and A is the pre-exponential factor. For integral methods the mathematical function that describe the reaction model is noted $g(\alpha)$.

The advanced non-linear isoconversional method (NLN) or Vyazovkin’s method [9,10,11,12] used in this study is presented in Equations (2) and (3) and has been derived from Equation (1):

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \quad (2)$$

$$J[E_\alpha, T(t_\alpha)] \equiv \int_{t_\alpha - \Delta\alpha}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT(t)}\right] dt \quad (3)$$

where E_α is the effective activation energy. The E_α value is determined as the value that minimizes the function $\Phi(E_\alpha)$ using a set of n experiments carried out under different arbitrary temperature programs $T_i(t)$ and uses a numerical integration of the integral with respect to the time. For each i -th temperature program, the time $t_{\alpha,i}$ and temperature $T_{\alpha,i}$ related to selected values of α are determined by an accurate interpolation using a Lagrangian algorithm [9,13]. Numerical integration is performed using trapezoidal rule. The method developed by N. Sbirrazzuoli and implemented in his internally generated software [9,13,14,15] can treat any kind of isothermal or non-isothermal data from DSC, calorimetry (C80), TGA, DMA, or rheometry [9,13,14,15,16]. This software was used in this study to compute a value of E_α for each value of α lying in between 0.02 to 0.98 with a step of 0.02. This advanced non-linear isoconversional method (NLN) was applied in this study.

Another isoconversional method can be derived by linearization of Equation (1) and is known as Friedman's method (FR) [13,17]:

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}} \quad (4)$$

Application of this method requires the knowledge of the reaction rate $(d\alpha/dt)_{\alpha,i}$ and of the temperature $T_{\alpha,i}$ corresponding to a given extent of conversion α for the i temperature programs used. The advantages of differential methods such as Friedman's method are that they use no approximations and can be applied to any temperature program. This does not hold for usual integral methods but is also the case for the nonlinear advanced isoconversional method previously described. Nevertheless, simulations have shown that differential isoconversional methods can sometimes reveal numerical instability [13], therefore before the use of Friedman method it was checked that the obtained results are consistent with those obtained with the NLN method.

2.2. Compensation effect

Model-free evaluation of the pre-exponential factor A_α and of the mathematical function $f(\alpha)$ that describes the reaction mechanism is not possible using Equations (2) and (4). Equation (4) permits the evaluation of the product $[A_\alpha f(\alpha)]$, thus if one needs to evaluate the pre-exponential factor A_α this will require the knowledge of the reaction mechanism, i.e. $f(\alpha)$. In order to determine A_α and $f(\alpha)$ in a model-free way, i.e. without introduction of the mathematical expression of $f(\alpha)$, the use of the so-called compensation effect has been

proposed [8,18,19,20,21,22]. This method is based on the experimental statement that for multi-step processes, the same experimental curve can be fitted by several reaction models. Transformation of Equation (1) into Equation (5) gives the mathematical justification of the apparent compensation effect that may exist when the model changes:

$$\ln A_i = \frac{E_i}{RT} + \ln \left[\frac{(d\alpha/dt)}{f(\alpha)} \right]_i = a E_i + b \quad (5)$$

where a and b are the compensation parameters and the subscript i refers to a factor producing a change in the Arrhenius parameters (conversion, temperature program). According to Equation (5) a pair of apparent parameters E_i and $\ln A_i$ can be computed using a model-fitting method, for each i reaction models $f(\alpha)$. Once the parameters a and b have been estimated the values of $\ln A_\alpha$ are evaluated using Equation (6):

$$\ln A_\alpha = a E_\alpha + b \quad (6)$$

The E_α values used in Equation (6) are obtained with an isoconversional method which leads to model-free values of A_α .

2.3. Reaction model

The differential form of the mathematical function that describe the reaction model, $f(\alpha)$ is determined according to Equation (7):

$$f(\alpha) = [A_\alpha f(\alpha)] / A_\alpha \quad (7)$$

where $[A_\alpha f(\alpha)]$ is obtained from the intercept of the Friedman plot (Equation 4) and $g(\alpha)$, the mathematical function that describe the reaction model for integral methods, is obtained from Equation (8) [9]:

$$G(\alpha) = g(\alpha) - g(\alpha - \Delta\alpha) = \int_{\alpha - \Delta\alpha}^{\alpha} \frac{d\alpha}{f(\alpha)} = A_\alpha J[E_\alpha, T(t_\alpha)] \quad (8)$$

2.4. Pre-exponential factor dependency for a multi-step process

For a multi-step processes, it is not possible to obtain an exact solution for the A_α -dependency in the general case. Isoconversional methods assume that a multi-step process can be described by a single-step equation of the form of Equation (9) if the computation is made for a given value of the extent of conversion [1,23]:

$$\left(\frac{d\alpha}{dt} \right)_\alpha = k_{ef,\alpha}(T) f_{ef,\alpha}(\alpha) = A_\alpha \exp\left(-\frac{E_\alpha}{RT_\alpha} \right) f_{ef,\alpha}(\alpha) \quad (9)$$

where $k_{ef,\alpha}$ is the effective (or apparent) rate constant and $f_{ef,\alpha}(\alpha)$ the reaction model computed for a constant α value. In this case, the hypothesis of a single-step process is only applied for each constant α value used for the computation, which corresponds, for nonisothermal data, to a very narrow temperature range, thus the assumption of the validity of a single-step equation for given α value generally hold even for complex reactions. This was demonstrated using simulated data and it was concluded that the single-step approximation is quite accurate for typical temperature ranges related to a given value of α [24].

For a multi-step reaction with two competing reactions, the overall reaction rate can be expressed as:

$$\frac{d\alpha}{dt} = k_1(T)f_1(\alpha) + k_2(T)f_2(\alpha) = k_{ef}(T)f_{ef}(\alpha) \quad (10)$$

In the peculiar case where $f_1(\alpha) = f_2(\alpha) = f_{ef}(\alpha)$ then

$$\frac{d\alpha}{dt} = [k_1(T) + k_2(T)]f_{ef}(\alpha) = k_{ef}(T)f_{ef}(\alpha) \quad (11)$$

$$\frac{d\alpha}{dt} = \left[A_1 \exp\left(-\frac{E_1}{RT}\right) + A_2 \exp\left(-\frac{E_2}{RT}\right) \right] f_{ef}(\alpha) = k_{ef}(T)f_{ef}(\alpha) \quad (12)$$

$$\left[A_1 \exp\left(-\frac{E_1}{RT}\right) + A_2 \exp\left(-\frac{E_2}{RT}\right) \right] = A_\alpha \exp\left(-\frac{E_\alpha}{RT}\right) \quad (13)$$

$$A_\alpha = \frac{A_1 \exp\left(-\frac{E_1}{RT}\right) + A_2 \exp\left(-\frac{E_2}{RT}\right)}{\exp\left(-\frac{E_\alpha}{RT}\right)} \quad (14)$$

Equation (14) gives the theoretical expression of the A_α -dependency for a model of two competing reactions with $f_1(\alpha) = f_2(\alpha)$. This Equation will be used to evaluate the accuracy of the computations of the A_α -dependency with the compensation method (CE) in association with an isoconversional method (FR or NLN).

2.5. Effective activation energy dependency for a multi-step process

The effective activation energy can be determined by taking the logarithmic derivative of the reaction rate at a constant extent of conversion. This is achieved by application of the isoconversional principle represented by Equation (15), to Equation (10) [3,11]:

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}} \right]_\alpha = \left[\frac{\partial \ln k(T)}{\partial T^{-1}} \right]_\alpha + \left[\frac{\partial \ln f(\alpha)}{\partial T^{-1}} \right]_\alpha = -\frac{E_\alpha}{R} \quad (15)$$

Then,

$$E_{\alpha} = -R \left[\frac{\partial \ln(d\alpha / dt)}{\partial T^{-1}} \right]_{\alpha} = \frac{E_1 k_1(T) f_1(\alpha) + E_2 k_2(T) f_2(\alpha)}{k_1(T) f_1(\alpha) + k_2(T) f_2(\alpha)} \quad (16)$$

$$E_{\alpha} = \frac{E_1 k_1(T) + E_2 k_2(T)}{k_1(T) + k_2(T)} \quad (17)$$

3. Data simulations

Simulated data were generated using a method described elsewhere [25] at four heating rates of 1, 2, 5 and 10 K.min⁻¹. A complex reaction involving two competing reactions was simulated using the following parameters: $A_1 = 339703.2279 \text{ s}^{-1}$, $E_1 = 60 \text{ kJ mol}^{-1}$, $f_1(\alpha) = (1 - \alpha)$, $A_2 = 178482139.8 \text{ s}^{-1}$, $E_2 = 80 \text{ kJ mol}^{-1}$, $f_2(\alpha) = (1 - \alpha)$. Compensation effect (CE) was performed using Achar-Brindley-Sharp (ABS) and Tang methods [9] in the interval $20 < \alpha < 80\%$ for the heating rate of 2 K.min⁻¹. Models 6, 7, 8 and 9 of reference [9] were selected as they lead to a correlation coefficient $r^2 \geq 0.99998$ for each model. The parameters of the CE using ABS methods were $a = 0.34863 \text{ mol. kJ}^{-1}$ and $b = -7.74462$ with $r^2 = 0.99984$. This method will be noted as CE(ABS). These parameters were also computed using the 18th models of reference [9] (excepted model 14 that was not used because it contains an adjustable parameter). In this case, $a = 0.32554 \text{ mol. kJ}^{-1}$, $b = -6.90838$ and $r^2 = 0.99933$. For the sake of comparisons, Tang method was also used. The CE parameters obtained were $a = 0.35083 \text{ mol. kJ}^{-1}$ and $b = -7.85599$ with $r^2 = 0.99972$. This method will be noted as CE(Tang). These parameters were used in the following to compute $\ln A_{\alpha}$ in a model-free way according to Equation (6). Then, $f(\alpha)$ was determined according to Equation (7) and $G(\alpha)$ was obtained from Equation (8).

4. Results

The simulated data are presented in Figure 1 in the form of $(d\alpha/dt)-T$ and $\alpha-T$ curves.

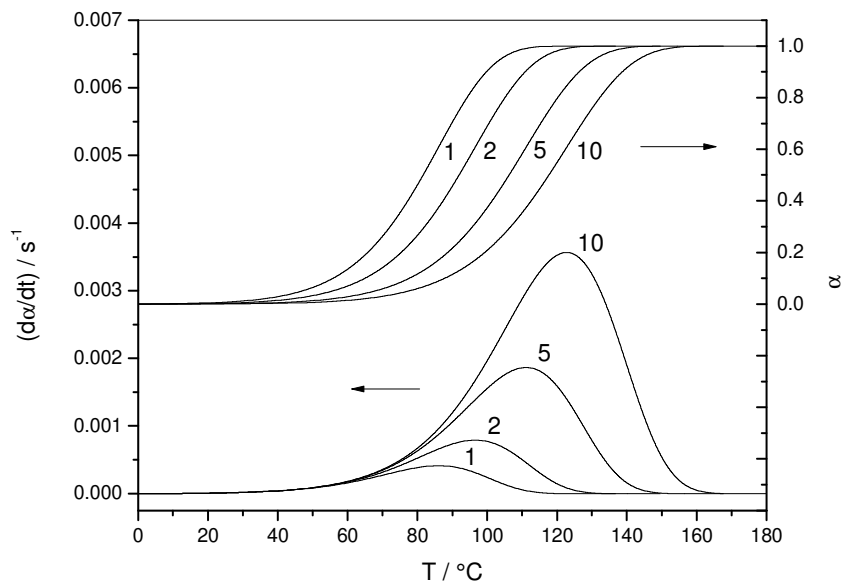


Figure 1. Simulated data for a multi-step process of two competing reaction. The heating rate is indicated by the line in $\text{K}\cdot\text{min}^{-1}$. Left $(d\alpha/dt)-T$ curves and right $\alpha-T$ curves.

Figure 2 gives the correlation obtained between $\ln A$ and E computed with CE(ABS) method. The values of $\ln A$ and E obtained for 18th models are also presented for comparisons. As expected a very good correlation between $\ln A$ and E is obtained when the “best” models (6,7,8,9) are used ($r^2 = 0.99984$). Interestingly, the values of the correlation coefficient is also close to one when all the models are used ($r^2 = 0.99933$) which attests to a good correlation between the parameters whatever the models used. This can lead to the conclusion that it is not necessary to proceed to the first stage of selection of the “best” models. Nevertheless, the use of these data to compute $\ln A$ and $f(\alpha)$ resulted in incorrect values (data not presented here).

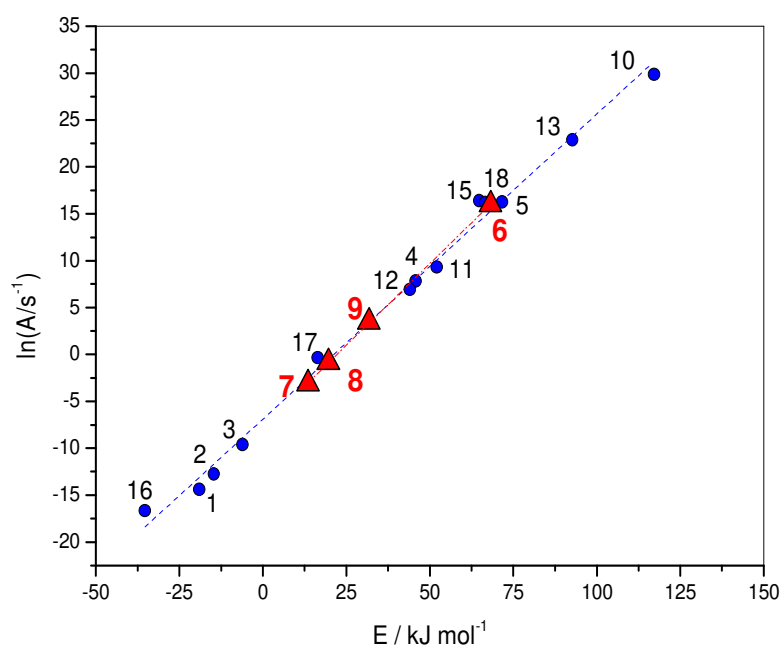


Figure 2. Compensation effect CE(ABS) for the 18th models of reference [9]. Logarithm of the pre-exponential factor ($\ln A$) as a function of activation energy (E) computed with ABS method. Triangle: values obtained for the selected models (6,7,8,9).

In the following the accuracy of the computation of A_α and $f(\alpha)$ in a model-free way will be determined as well as the differences resulting of the use of FR, NLN, ABS or Tang methods. The methods will be noted FR-ABS, NLN-ABS and NLN-Tang. The first term corresponds to the method used for the estimation of E_α and the second term to the method used for the CE. Figure 3 presents the theoretical values of the logarithm of the pre-exponential factor ($\ln A_\alpha$ obtained from Equation 14) as a function of temperature (T) and extent of conversion (α) and the results obtained for the $\ln A_\alpha$ -dependency using NLN-ABS.

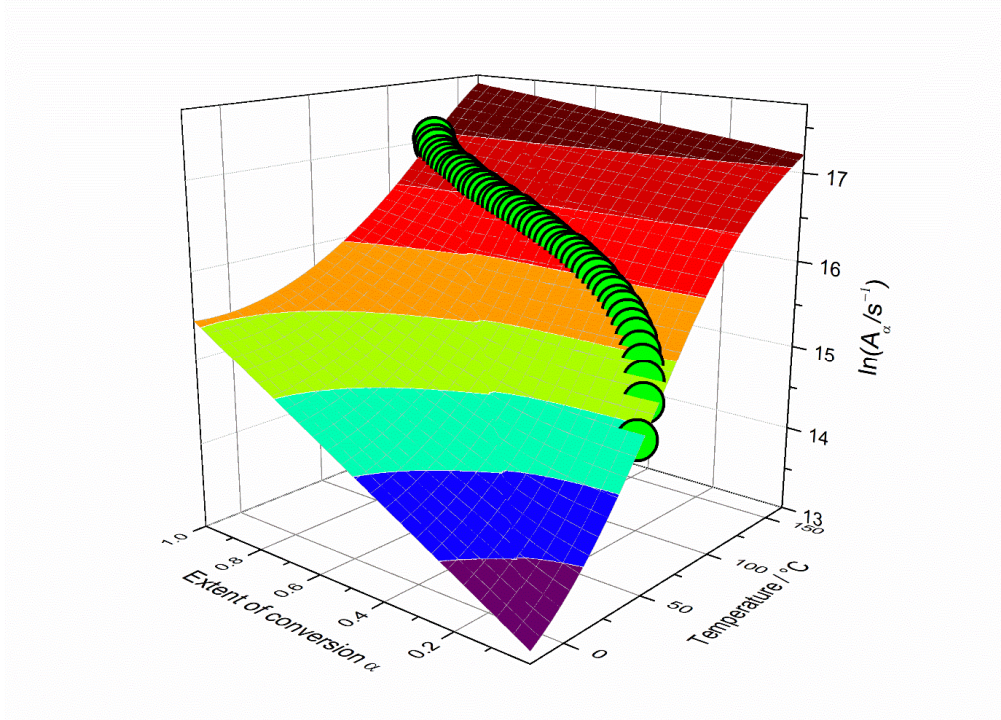


Figure 3. Simulated values of the theoretical $\ln A_\alpha$ -dependency with temperature (T) and extent of conversion (α). Open circle: $\ln A_\alpha$ -dependency obtained for 1, 2, 5 and 10 $\text{K}\cdot\text{min}^{-1}$ using NLN-ABS method.

To evaluate the accuracy of the method the reference values of A_α were computed according to Equation (14) and compared to the data obtained using CE and an isoconversional method. The results are presented in Figure 4. The values of the E_α -dependencies computed with FR and NLN are presented in the inset of Figure 4 and compared to the reference values obtained from Equation (17). Three different methods were compared, i.e. FR-ABS, NLN-ABS and NLN-Tang. The results indicate that all the methods give very accurate values for the $\ln A_\alpha$ -dependency obtained using CE method. It is interesting to note that even if the CE parameters were evaluated for a limited interval of $20 < \alpha < 80\%$ we do not observe large deviations of the $\ln A_\alpha$ -dependency for values outside of this interval. Nevertheless, it is not possible to generalize this conclusion to the case where $f_1(\alpha) \neq f_2(\alpha)$.

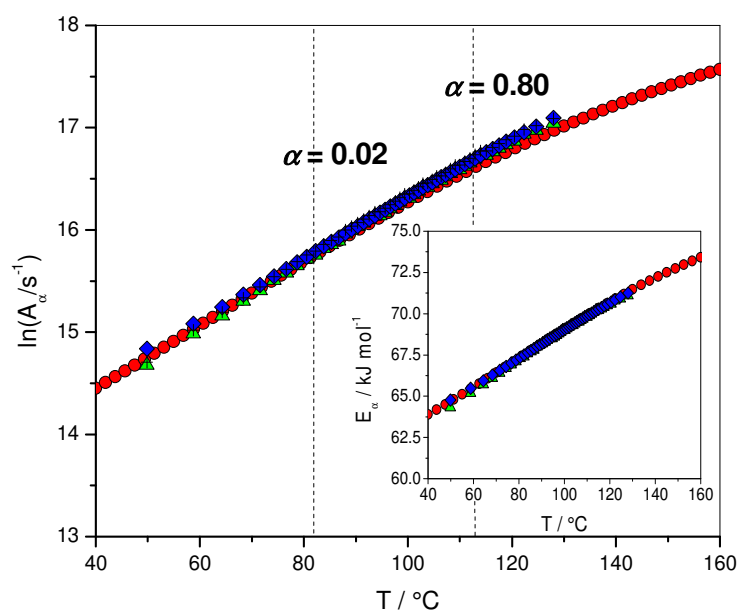


Figure 4. $\ln A_\alpha$ -dependency with temperature (T). Circle: reference values (Eq. (14)), triangle: values obtained using NLN-ABS method, diamond: values obtained using FR-ABS method, cross: values obtained using NLN-Tang method. Inset: E_α -dependency with temperature (T). Circle: reference values (Eq. (17)), triangle: NLN method, diamond: FR method.

Table 1 gives the relative errors on the logarithm of the pre-exponential factor ($\ln A_\alpha/s^{-1}$) for the three methods. The use of the Tang integral method for CE is more suitable when the integral isoconversional method NLN is applied. The lowest errors are obtained with NLN-Tang method. Surprisingly, the mean relative error is lower when all the data are used with FR-ABS (including the values outside of the interval used for the CE), while it is the opposite with NLN (for NLN-ABS and NLN-Tang). Nevertheless, the difference is probably not significant. All the methods give an error less than 1% and thus, it is concluded that they are suitable for the determination of $\ln A_\alpha$ in a model-free way.

Table 1. Relative errors on the logarithm of the pre-exponential factor ($\ln A/s^{-1}$)

α	$RE(\ln A)$ FR-ABS ^a	$RE(\ln A)$ NLN-ABS ^b	$RE(\ln A)$ NLN-Tang ^c
0.02	0.0026	0.0133	0.0113
0.10	0.0070	0.0106	0.0084
0.20	0.0070	0.0093	0.0070
0.50	0.0054	0.0053	0.0028
0.80	0.0029	0.0033	0.0007
0.98	0.0001	0.0029	0.0003
Mean ($0.02 < \alpha < 0.98$)	0.42%	0.75%	0.51%
Mean ($0.2 < \alpha < 0.80$)	0.51%	0.59%	0.35%

- a) Relative error using CE(ABS) and FR method, CE parameters computed for $0.2 < \alpha < 0.80$
- b) Relative error using CE(ABS) and NLN method, CE parameters computed for $0.2 < \alpha < 0.80$
- c) Relative error using CE(Tang) and NLN method, CE parameters computed for $0.2 < \alpha < 0.80$

The mathematical function $f(\alpha)$ that describes the reaction mechanism was computed using FR-ABS method and Equation (7). The resulting values are presented in Figure 5 and show the very good agreement between computed values and reference values (model 6). Normalized functions $f(\alpha)/f(\alpha)_{\max}$ were represented in Figure 5 for more clarity. Each function was simply divided by the highest value found in the interval of computation.

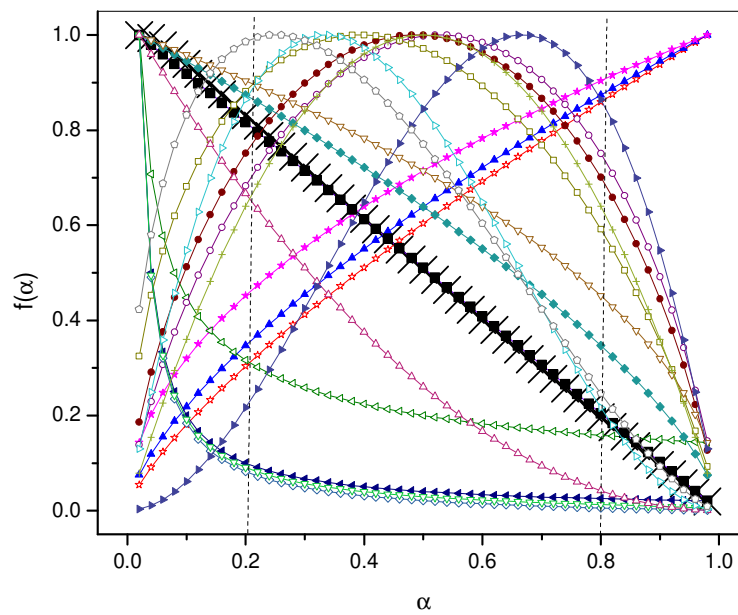


Figure 5. Variation of the normalized function $f(\alpha)/f(\alpha)_{\max}$ with extent of conversion (α) for the 14 reference models (1: open stars, 2: solid up triangles, 3: solid stars, 4: open left triangles, 5: solid left triangles, 6: solid squares, 7: open circles, 8: solid circles, 9: open squares, 10: open diamonds, 11: solid diamonds, 12: open down triangles, 13: solid down triangles, 14: open up triangles, 15: open right triangles, 16: solid right triangles, 17: cross (+), 18: open pentagone). Cross (x): $f(\alpha)/f(\alpha)_{\max}$ value obtained using FR-ABS method at 2 K.min^{-1} .

The same conclusion apply for the determination of $G(\alpha)$ using NLN-Tang method and Equation (8) as shown in Figure 6. Normalized functions $G(\alpha)/G(\alpha)_{\max}$ were represented in Figure 6 for more clarity. Each function was simply divided by the highest value found in the interval of computation.

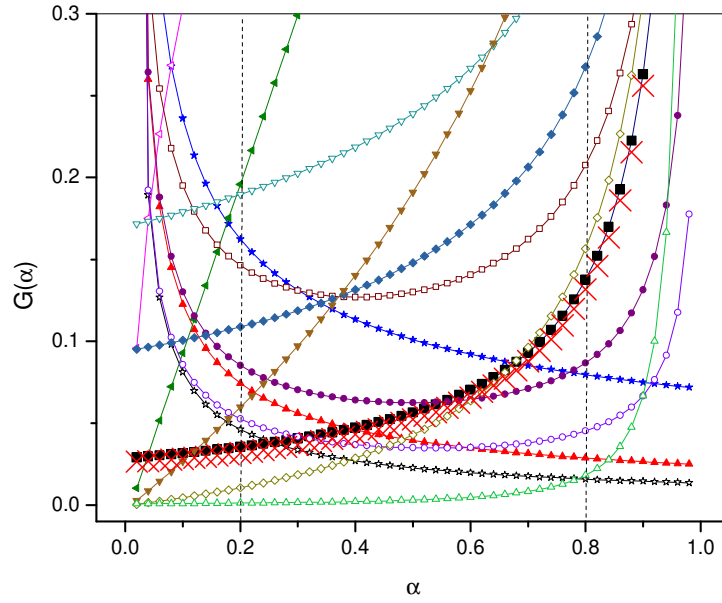


Figure 6. Variation of the normalized function $G(\alpha)/G(\alpha)_{\max}$ with extent of conversion (α) for the 14 reference models (1: open stars, 2: solid up triangles, 3: solid stars, 4: open left triangles, 5: solid left triangles, 6: solid squares, 7: open circles, 8: solid circles, 9: open squares, 10: open diamonds, 11: solid diamonds, 12: open down triangles, 13: solid down triangles, 14: open up triangles). Cross (x): $G(\alpha)/G(\alpha)_{\max}$ values obtained using NLN-Tang method at $2 \text{ K}\cdot\text{min}^{-1}$.

Table 2 gives the relative errors on $f(\alpha)$ and $G(\alpha)$ obtained with FR-ABS, NLN-ABS and NLN-Tang. The lowest errors are obtained for FR-ABS with around 2-3% instead of around 6-8% for the two other methods. According to the results of Table 1, NLN-Tang method gives the lowest errors for the evaluation of $\ln A_\alpha$, while the lowest errors for the reaction model are obtained using FR-ABS (Table 2). Thus, it is proposed to compute $f(\alpha)$ using the reaction rate evaluated at $2 \text{ K}\cdot\text{min}^{-1}$ for each α divided by the rate constant $k_\alpha(T)$ and NLN-Tang method, to avoid the use of Equation (8). Indeed, the Arrhenius rate constant can be obtained from Equation (18):

$$k_\alpha(T) = A_\alpha \cdot \exp(-E_\alpha / RT_\alpha) \quad (18)$$

Then, $f(\alpha)$ can be obtained from Equation (19):

$$f(\alpha) = (d\alpha / dt)_\alpha / k_\alpha(T) \quad (19)$$

This method is referred as NLN-Tang-R and the results are presented in Table 2. As expected this method leads to the lowest errors for the determination of the mathematical function that describe the reaction model $f(\alpha)$. A value of 0.28% is obtained in this case for NLN-Tang-R,

much lower to the value of 2.26% obtained with FR-ABS. The difference observed between the computations performed using the whole extent of conversion interval and the interval used for the CE method is weak. Evaluation of $G(\alpha)$ always lead to higher errors. Thus, it is recommended to compute $f(\alpha)$. Finally, it can be concluded that the CE method in association with an advanced isoconversional method allows for the determination of A_α and $f(\alpha)$ in a model-free way with a high accuracy.

Table 2. Relative errors on $f(\alpha)$ and $G(\alpha)$

α	$RE [f(\alpha)]$ FR-ABS ^a	$RE [G(\alpha)]$ NLN-ABS ^b	$RE [G(\alpha)]$ NLN-Tang ^c	$RE [f(\alpha)]$ NLN-Tang-R ^d
0.02	0.0000	0.0716	0.0854	0.0000
0.10	0.0225	0.1003	0.1096	0.0072
0.20	0.0183	0.0975	0.1048	0.0062
0.50	0.0080	0.0729	0.0772	0.0021
0.80	0.0417	0.0408	0.0430	0.0002
0.98	0.0867	0.0000	0.0000	0.0041
Mean (0.02 < α < 0.98)	2.95%	6.38%	7.00%	0.33%
Mean (0.2 < α < 0.80)	2.26%	7.04%	7.50%	0.28%

a) Relative error using CE(ABS) and FR method, CE parameters computed for $0.2 < \alpha < 0.80$

b) Relative error using CE(ABS) and NLN method, CE parameters computed for $0.2 < \alpha < 0.80$

c) Relative error using CE(Tang) and NLN method, CE parameters computed for $0.2 < \alpha < 0.80$

d) Relative error using CE(Tang), NLN method and Eq. (19), CE parameters computed for $0.2 < \alpha < 0.80$

5. Conclusion

Several methods to evaluate the pre-exponential factor A_α and the mathematical function that describe the reaction model $f(\alpha)$ in a model-free way were proposed. Three different methods were applied to simulated data of a multi-step process, i.e. FR-ABS, NLN-ABS, NLN-Tang. The results indicate that all the methods give very accurate values. For the evaluation of $\ln A_\alpha$ the lowest errors are obtained with NLN-Tang (0.35%) and FR-ABS (0.51%). For the evaluation of $f(\alpha)$ the lowest errors are obtained with a modification of the NLN-Tang method referred as NLN-Tang-R (0.28%) and FR-ABS (2.26%). Evaluation of the integral form of the reaction model always lead to higher errors, but lower than 8%. The complementary of the information gained with the knowledge of the pre-exponential factor and function related to the reaction mechanism in addition with the effective activation energy, E_α can be very efficient for the elucidation of complex reaction mechanisms in the condensed phase. It was shown that the methods proposed in this work could be used for this purpose.

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TABLE OF CONTENT IMAGE

The effective activation energy (E_a) dependency is used to compute the dependence of the pre-exponential factor (A_a) and of the mathematical function that describe the reaction mechanism $f(\alpha)$ in a model-free way. The effective rate constant $k_a(T)$ depends on both temperature (T) and extent of conversion (α) for multi-step reactions in nonisothermal mode.

