

Letter to the Editor

Additional considerations to the paper entitled: “Computational aspects of kinetic analysis. Part B: The ICTAC Kinetics Project—the decomposition kinetics of calcium carbonate revisited, or some tips on survival in the kinetic minefield.”

Abstract

Dr. Marek Maciejewski reported in 1999 in an excellent work the second part of a series of papers dealing with the results of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) Kinetic Analysis Project [M.E. Brown, M. Maciejewski, S. Vyazovkin, R. Nomen, J. Sempere, A. Burnham, J. Opfermann, R. Strey, H.L. Anderson, A. Kemmler, R. Keuleers, J. Janssens, H.O. Desseyn, C.-R. Li, T.B. Tang, B. Roduit, J. Malek, T. Mitsuhashi, *Thermochim. Acta* 355 (2000) 125–143; M. Maciejewski, *Thermochim. Acta* 355 (2000) 145–154; S. Vyazovkin, *Thermochim. Acta* 355 (2000) 155–163; A.K. Burnham, *Thermochim. Acta* 355 (2000) 165–170; B. Roduit, *Thermochim. Acta* 355 (2000) 171–180]. In this work Dr. Maciejewski emphasized the very limited applicability of the kinetic methods that use single-heating rate data and stated that to obtain reliable kinetic descriptions, computational methods that employ multi-heating rate data should be used for treating multi-step processes. The reasons supporting this argument are presented in his “Fact 2”, where it was stated that two different models represent very similar α - T curves at one heating rate (5 °C/min), but at other two different heating rates (2 and 10 °C/min) the same kinetic parameters used at 5 °C/min illustrate very different curves. In this letter to the editor, we show different examples where we intend to illustrate that interactions among parameters are even higher than this author described, since there is a possibility that different models, could be able to reproduce the same conversion curves at different heating rates simultaneously.

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Keywords: Kinetic analysis; Kinetic models

Dr. Marek Maciejewski reported in 1999 in an excellent work the second part of a series of papers dealing with the results of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) Kinetic Analysis Project [1–5]. We fully agree with most of the contents of the paper that was presented in a very didactical way and wonder why still many authors keep on falling into the same errors and mistakes pointed out in this paper and in many others.

We believe that it is worth mentioning some of Maciejewski’s statements:

1. Model fitting methods based on a multi-step process can be very useful for describing the course of solid reactions.
2. The physical meaning of the kinetic triplet (kinetic constant, activation energy and conversion degree function) should be analyzed very carefully. Although many authors tend to analyze uniquely one kinetic parameter (mainly E_a), it is generally incorrect, since the whole reaction pattern depends on the kinetic model used and its corresponding conversion degree function $f(\alpha)$, the characteristic parameter of the kinetic model (for example, the reaction order of the n -order

reaction model), the activation energy (E_a) and the preexponential factor (A). Only one of them cannot be used to compare processes.

Nevertheless, in this work Dr. Maciejewski emphasized the very limited applicability of the kinetic methods that use single-heating rate data and stated that to obtain reliable kinetic descriptions, computational methods that employ multi-heating rate data should be used for treating multi-step processes. The reasons supporting this argument are presented in his “Fact 2”, where it was stated that two different models represent very similar α - T curves at one heating rate (5 °C/min), but at other two different heating rates (2.5 and 10 °C/min) the same kinetic parameters used at 5 °C/min illustrate very different curves. In order to quantify the degree of similarity of both curves and to have a reference of what could be considered a good fitting, a variation coefficient (V.C.) has been calculated by the next procedure. We have integrated kinetic equations by the fourth order Runge–Kutta method, using the parameters and models reported. Then, the variation coefficient has been obtained from the squared differences between conversions obtained from both

Table 1
Kinetic models and nomenclature used

Model	Symbol	$f(\alpha)$
Reaction order model	F_n	$(1 - \alpha)^n$
Sestaké–Berggren (empirical kinetic model)	SB_{nm}	$\alpha^n(1 - \alpha)^m$
Random nucleation and growth of nuclei (Avrami–Erofeev equation)	A_n	$n(1 - \alpha)[- \ln(1 - \alpha)]^{(1-1/n)}$

models, the number of data (N) and the average of the conversion degree $\bar{\alpha}$:

$$\text{V.C.} = \sqrt{\frac{\sum_i (\alpha_{i \text{ model 1}} - \alpha_{i \text{ model 2}})^2}{N \bar{\alpha}^2}} \quad (1)$$

Since the exact parameters used by Maciejewski were unknown for us, kinetic parameters for the D3 model (Jander equation) have been optimized by minimizing the following objective function:

$$\text{O.F.} = \sum (\alpha_i^{\text{FN}} - \alpha_i^{\text{D3}})^2 \quad (2)$$

where α_i^{FN} and α_i^{D3} are, respectively, the conversion degrees calculated for the reaction order model and the Jander equation at 5 °C/min. Kinetic parameters calculated were $E_a = 308.000$ kJ/mol, $\ln A = 29.4781$ for the D3 model. The variation coefficient obtained was 2×10^{-4} .

Other authors use this reasoning to discard the possibility of using a set of single heating rate data to obtain kinetic parameters. For example, Budrugaec and Segal [6], assumed such a high grade of interaction among kinetic parameters and use the IKP method (which is based on this fact, i.e. the high degree of interaction among kinetic parameters) in the conversion range 0.05–0.90. In Table 3 of their work, the authors show kinetic parameters and models which are supposed to reproduce very similar conversion degree curves. For example, the reaction order model (Table 1), with two different reaction orders $F_{0.6}$ and F_1 (the model F_n with $n = 0.6, 1$) and different pre-exponential factors and activation energies seems to reproduce the same conversion degree curves in that interval (the corresponding V.C. was 0.015), although if considering the whole interval, i.e. $\alpha = 0-1$, it is evident that differences are substantially higher (i.e. V.C. = 0.018), as shown, for example, in Fig. 1 for two of these models ($F_{0.6}$ and F_1). More relevant differences and higher V.C. could have been obtained if $F_{0.6}$ and $F_{1.7}$ had been compared. These models, with the appropriate set of kinetic parameters, were also considered as equivalent by these authors. Hence, the variation coefficient for a good fitting could be considered to reach values of the order of 10^{-4} to 10^{-2} .

Obviously, if ranges studied are reduced even more, for example, in cases where there are complex reactions patterns and it is necessary to employ a narrower conversion range, the amount of models capable to reproduce very similar conversion behaviors may be is still higher.

Thus, in order to avoid parameter interactions and the possibility that different sets of kinetic parameters could represent very similar conversion curves, these and other authors strongly recommend that kinetic analysis of single heating rate experiments should be generally avoided. With the following examples, we intend to illustrate that interactions among parameters are even higher than these authors described, since there is a possibility that different models, with different kinetic parameters could be able to reproduce very similar conversion curves at different heating rates simultaneously. Consequently, and following the same type of reasoning, kinetic modeling could not be used as a tool of model validation, i.e. a good fit of experimental data at different heating rates is an important, but not the unique, requirement to ask to a model.

In this work, we present some examples that support the latter statements. For this purpose, kinetic models listed in Table 1 have been employed and compared by using different sets of kinetic parameters at the three heating rates reported by Maciejewski.

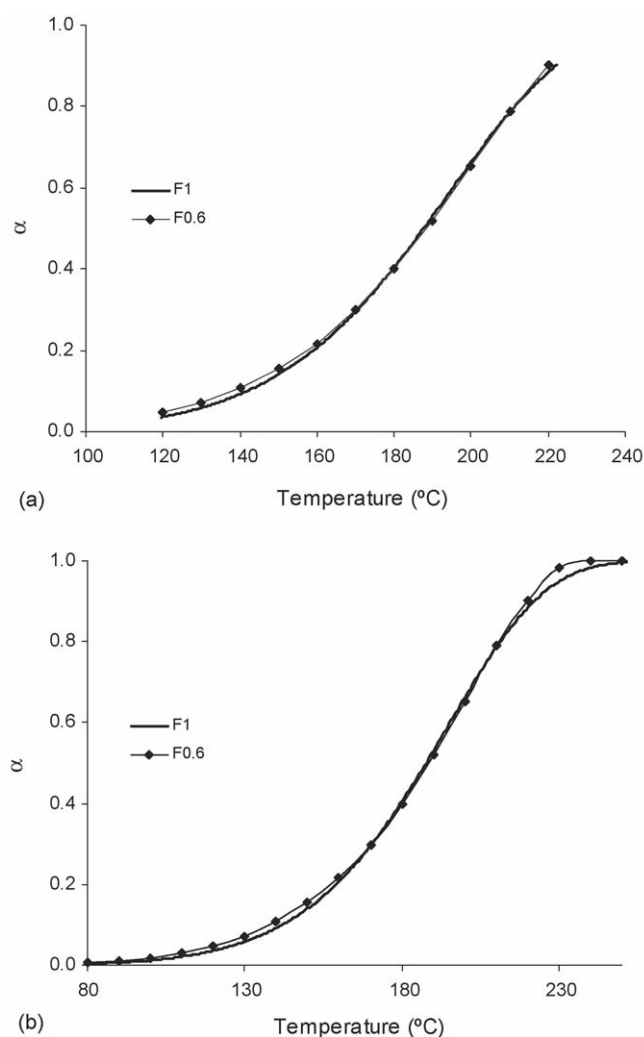


Fig. 1. Conversion curves calculated with models $F_{0.6}$ and F_1 using kinetic parameters reported by Budrugaec and Segal at 0.5 °C/min (a) in the conversion range employed by these authors and (b) in the whole conversion range.

1. Case 1: the nucleation and the reaction order models

First of all, it is worth mentioning that F_n and A_n models (Table 1) may represent very similar conversion curves. In fact, by setting n equals to 1 in the two corresponding expressions, the same functions are obtained, as shown below.

Random nucleation and growth of nuclei ($n = 1$):

$$\begin{aligned} f(\alpha) &= n(1 - \alpha)[- \ln(1 - \alpha)]^{(1-1/n)} \\ &= 1(1 - \alpha)[- \ln(1 - \alpha)]^{(0)} = 1 - \alpha \end{aligned} \quad (3)$$

Reaction order model ($n = 1$):

$$f(\alpha) = 1 - \alpha \quad (4)$$

Thus, independently of the values of activation energy, pre-exponential factor and heating rate, both models will give, when $n = 1$, the same conversion degree curves. Obviously it is a consequence of the mathematical expression, but it is important to have in mind that eventually both models, with a different physical meaning, have the same mathematical shape.

There exists certain sets of preexponential factor, activation energy and reaction orders, where both models predict similar curves of conversion degrees for different heating rates and the whole conversion degrees interval.

In order to illustrate this fact, a set of curves have been generated using the reaction order model with parameters reported in Table 2 at different heating rates ($\beta = 2.5, 5$ and 10 K/min), integrating by the fourth order Runge–Kutta procedure the following equation:

$$\alpha = \int_0^T A e^{+E/RT} \frac{f(\alpha)}{\beta} dT = \int_0^t A e^{+E/RT} f(\alpha) dt \quad (5)$$

We have found a set of kinetic parameters for the nucleation model equation (Table 1) which yield a conversion curve very similar to that calculated by the F_n model at different heating rates, as it is possible to observe in Fig. 2. The variation coefficients calculated from data in the whole conversion range are quite low, showing a high degree of coincidence between both models: a variation coefficient of 1×10^{-5} for the 5 K/min curve and approximately 0.002 for the others. The latter variation coefficients lie between those calculated from data of Budrugaec and Segal and that calculated from Maciejewski models, while the first one is much lower. Consequently in this case, the two models tested at three heating rates should also be considered equivalent and thus (following the same reasoning of Budrugaec and Segal) invalidating the analysis at different heating rates.

Table 2
Kinetic parameters calculated for the F_n and A_n models

	F_n	A_n
$\ln A$ (s^{-1})	19.0	17.84
E_a (kJ/mol)	125.0	119.3
n	1	1.04

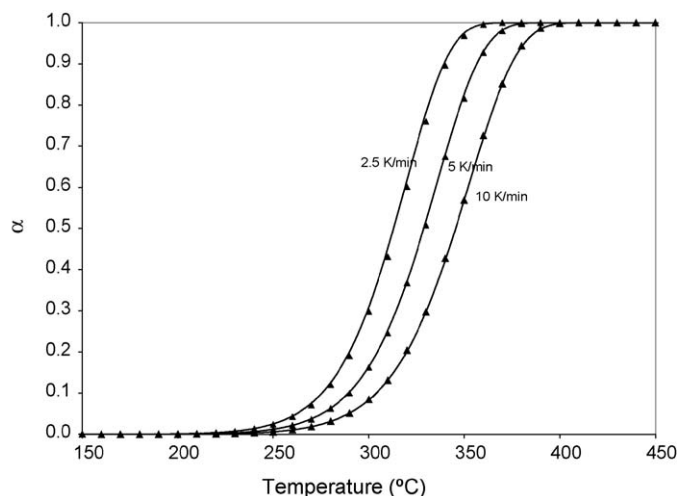


Fig. 2. Conversion curves calculated with models: (—) F_n and (\blacktriangle) A_n at different heating rates between 2.5 and 10 K/min calculated from kinetic parameters of Table 2.

2. Case 2: the nucleation and the Sestake–Bergren models

Following the same procedure, some reference curves were generated using the A_n model with kinetic parameters shown in Table 3. Moreover, other model, as the Sestake–Bergren, was considered. As it is possible to observe in Fig. 3, there is a set of kinetic parameters (Table 3) which makes possible to obtain conversion degree curves very similar. Variation coefficients calculated

Table 3
Kinetic parameters calculated for the A_n and the SB_{nm} models

	A_n	SB_{nm}
$\ln A$ (s^{-1})	22.0	20.67
E_a (kJ/mol)	125.0	115.6
n	2	0.79
m	–	0.54

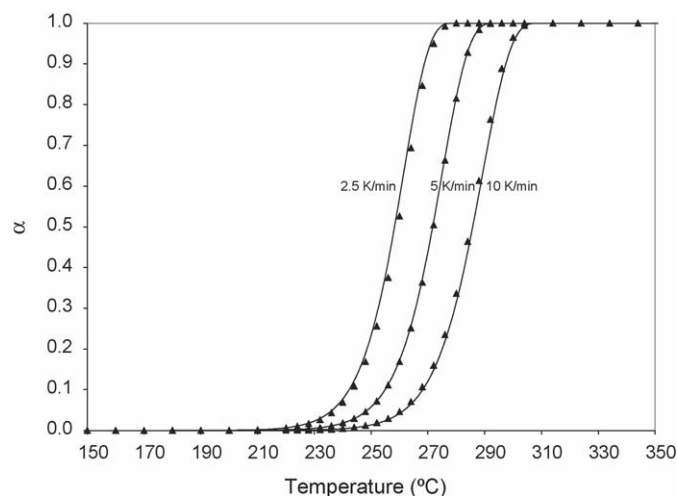


Fig. 3. Conversion curves calculated with models: (—) SB_{nm} and (\blacktriangle) A_n at different heating rates between 2.5 and 10 K/min.

culated were 1×10^{-4} for the 5 K/min curve and approximately 0.004 for the others. Similarly to the previous case, these low values reveal again a high grade of coincidence between both models.

Similar conclusions can be obtained comparing F_n and SB_{nm} models with different values of n and m .

3. Case 3: overlapped processes

Lets us consider another type of hypothetical situation where a product A can decompose via two different reactions, as may occur during polymers degradation, and 50% of A follows the first route, while 50% the second route:



and reactions 1 and 2 are described by the reaction order model. Although their corresponding kinetic parameters are different (Table 4), both processes are not easily separated by changing the heating rate, as possible to observe in Fig. 4.

A mere analysis of the overall conversion degree curve or alternatively its derivative could reveal that only one process is taking place (see Fig. 5), i.e.:



The kinetic analysis of these curves can be achieved by considering one single step and the reaction order model. For example, there exists a set of kinetic parameters ($\ln A(s-1) = 10.62$, E_a (kJ/mol) = 98.8, $n = 1.38$) that allows a very good fit of the conversion degree curves, as is possible to observe in Fig. 5.

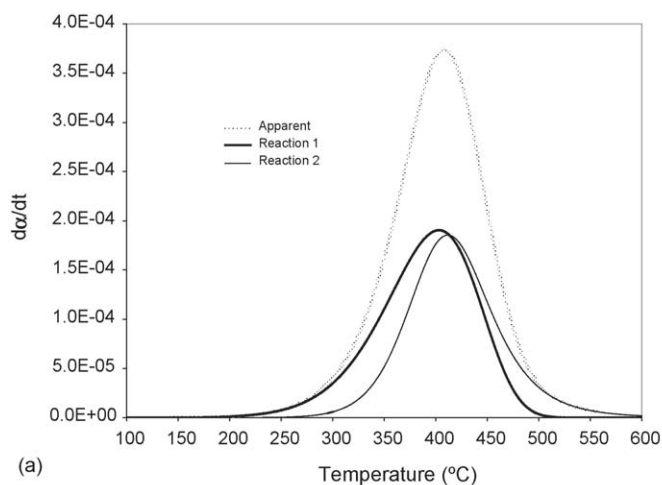
Are in consequence the mechanism and the model suggested valid (i.e. one single step with the reaction order model)?

In our opinion kinetic analysis cannot be used uniquely to validate models or reaction mechanisms. A good fit of experimental results is only one condition, but it should not be the unique one. Other techniques, as for example, infrared or mass spectroscopy can be useful in order to obtain more information about processes involved. In this example, the monitoring of likely signals attributed to B and C could have revealed that they are not released concurrently and the suggested single step mechanism is wrong.

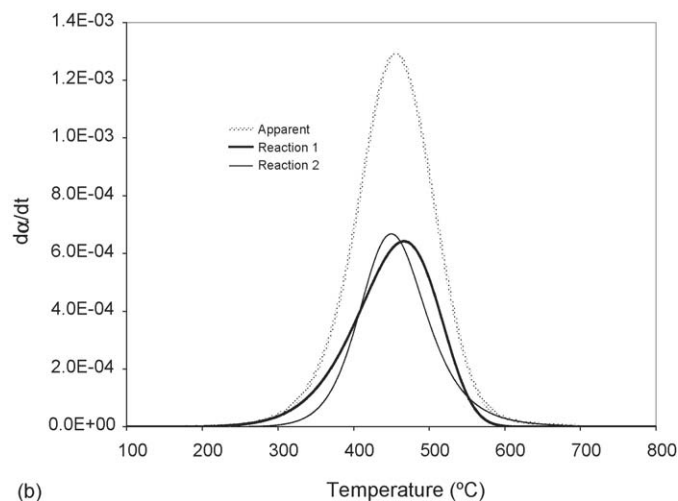
However, this practice is very common in polymer degradation, where it is well known that pattern mechanisms are very complicated and can follow many different and simultaneous routes. In this case, apparent kinetic parameters are obtained in order to reproduce experimental curves at different heating rates with other different purposes that mechanism validation

Table 4
Kinetic parameters for processes considered with the model F_n

	Step 1	Step 2
$\ln A$ (s^{-1})	7.00	17.55
E_a (kJ/mol)	79.0	137.2
n	1	2



(a)



(b)

Fig. 4. Weight loss derivative for steps 1 and 2 and the overall process at: (a) 2.5 K/min and (b) 10 K/min.

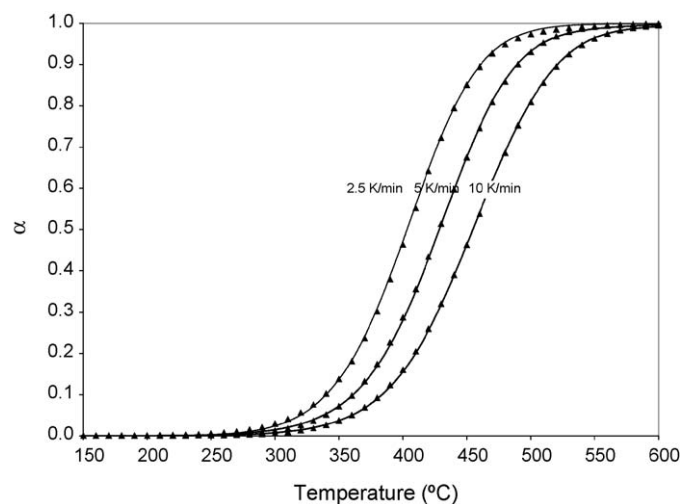


Fig. 5. Conversion degree curves of the apparent process generated with two overlapped processes (—) and calculated considering one single step (▲).

(for example, the calculation of apparent kinetic parameters for reactors design). In this case, kinetic parameters should not be asked to have physical meaning, since their role is only to make possible reproducing experimental weight loss curves in the conditions employed.

4. Discussion

Different models are capable to correlate a set of dynamic conversion data obtained at different heating rates.

The question that rises is: does this fact invalidates the kinetic analysis of data at different heating rates, as the widely accepted similar argument seems to do it in the case of data obtained at a single heating rate?

We believe that considering data at different heating rate is better than treating them at a single heating rate, but none of the two possibilities guarantee the validation of a kinetic model in the mechanistic sense. We believe that the capability of a model to represent a set of data (either at a single or at multiple heating rates) is a necessary but not sufficient condition to validate a kinetic model. In other words, conversion curves obtained, for example, directly from weight loss data seems to be incomplete data to assess mechanistic results. To attain such a goal, thermogravimetric data must be complemented with other type of techniques. The analysis of the gases evolved or the analysis of the solid fraction remaining would be considered among other possibilities. Nevertheless, thermogravimetric data fitting at different rates is a powerful tool to discard pseudokinetic models in order to determine apparent kinetic parameters capable of simulate the weight loss processes under conditions similar to those present in the thermogravimetric equipment.

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