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The abuse of the Harcourt and Esson relationship in interpreting the kinetics of rising temperature solid state reactions

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Abstract

The literature proposal of using the Harcourt and Esson approach for determining the activation energy as a function of the conversion from a single non-isothermal experiment has been reanalyzed. It has been shown that the kinetic equation resulting from this approach was not properly derived. It has been demonstrated that the use of this approach necessarily leads to an apparent linear increase of the activation energy with the temperature independently that the activation energy would be either constant or a function of the conversion. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The kinetic analysis of solid state reactions from TG and DTG data recorded under non-isothermal conditions became very popular from the earlier proposals by Kissinger [1], Freeman and Carroll [2], Coats and Redfern [3] and Zakó [4] of formal kinetic equations to be used for this purpose. The popularity of the non-isothermal methods with regards to the isothermal ones rests on the assumption that the reaction kinetic parameters can be determined from a single non-isothermal experiment while isothermal methods require a set of experiments at different temperatures. However, it has been pointed out in previous papers [5–9] that both the kinetic parameters and the kinetic model obeyed by the reaction cannot be simultaneously discriminated from a single experiment. This conclusion has been confirmed in a recent paper [10] that redefine the master plots based on the integral and/or differential forms of the kinetic equations describing solid state reactions by using the concept of generalized time introduced by Ozawa [11–13]. This redefinition permits the application of these master plots to the kinetic analysis of solid state reactions, whatever the type of temperature program used for collecting the experimental data. It has been shown that in isothermal conditions a single curve is enough to construct the experimental master plots, while in non-isothermal conditions, the knowledge of both the conversion as a function of temperature and activation energy is required for matching the master plot curves from experimental data. This means that it is quite impossible to discriminate the kinetic model fitted by the reaction from a single TG or DTG curve without a previous knowledge of the activation energy. This parameter would be previously determined, for instance, from a set of non-isothermal curves recorded under different heating rates using isoconversional methods [11,14,15]. Dollimore and co-workers

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[16–19] have recently proposed a new method of kinetic analysis that is being regularly used by a number of authors [20–24] and has been collected in recent reviews on the topic [25,26]. Dollimore and co-workers have concluded that the kinetic analysis of a single non-isothermal experiment permits not only determining the kinetic model and the activation energy [17,27,28] but even the variation of this last parameter as a function of the conversion [17]. This statement seems to be in contradiction with previous ones and, therefore, would deserve a detailed analysis.

2. Theoretical

The reaction rate of a solid state reaction can be expressed in the form

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

where α is the reacted fraction at the time t, T the absolute temperature, $f(\alpha)$ the function depending of the kinetic law obeyed by the reaction and k is the constant rate that is generally expressed by the Arrhenius law

$$k = A\,e^{-E/RT} \tag{2}$$

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

Eqs. (1) and (2) lead to

$$\frac{d\alpha}{dt} = A\,e^{-E/RT} f(\alpha) \tag{3}$$

If the process is recorded under a linear heating rate $\beta = dT/dt$, Eq. (3) would be rewritten in the form

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\,e^{-E/RT} f(\alpha) \tag{4}$$

Integration of Eq. (4) leads to

$$g(\alpha) = \int_0^{\alpha} \frac{1}{f(\alpha)}\,d\alpha = \frac{A}{\beta}\int_0^T e^{-E/RT}\,dT \tag{5}$$

The integral of the right-hand side of Eq. (5) can be expressed in the form

$$\int_0^T e^{-E/RT}\,dT = \frac{E}{R}\int_{\infty}^{x} \frac{e^{-x}}{x^2}\,dx = \frac{E}{R}p(x) \tag{6}$$

where $x = E/RT$.

The $p(x)$ function cannot be expressed in a closed form but can be calculated by using different approximations. It has been shown in a recent paper [29] that the following rational approach of fourth order, formerly proposed by Senum and Yang [30] and corrected by Flynn [31]:

$$p(x) = \frac{e^{-x}}{x}\,\frac{x^3 + 18x^2 + 86x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{7}$$

allows to calculate the $p(x)$ function with an accuracy better than $10^{-5}\%$ for x-values higher than 5.

A number of authors have recently [32,33] expressed the constant rate in terms of power series. The simplest of these series is given by the Harcourt and Esson [34] relationship

$$k = CT^m \tag{8}$$

where C and m are constants (m is positive) that have not a defined physical significance.

The combination of Eqs. (1) and (8) lead to

$$\frac{d\alpha}{dT} = \frac{CT^m}{\beta} f(\alpha) \tag{9}$$

that would be integrated in the form

$$g(\alpha) = \frac{C}{\beta(m+1)} T^{m+1} + D \tag{10}$$

D being an integration constant.

A method that pretends to determine the activation energy as a function of α from a single TG curve by using the Harcourt and Esson approach has been recently proposed by Dollimore et al. [17]. This method implies to determine firstly the coefficient m from the slope of the plot of either $\log[(d\alpha/dT)/f(\alpha)]$ or $\log g(\alpha)$ as a function of $\log T$ according to Eqs. (9) and (10), respectively, and, secondly, to consider the identity of the two approaches expressed by Eqs. (2) and (8). Then they write for temperature T_1

$$k_{T_1} = CT_1^m = A\,e^{-E/RT_1} \tag{11}$$

and at temperature T_2

$$k_{T_2} = CT_2^m = A\,e^{-E/RT_2} \tag{12}$$

when

$$\left[\frac{T_2}{T_1}\right]^m = \frac{e^{-E/RT_2}}{e^{-E/RT_1}} \tag{13}$$

or

$$m \ln \frac{T_2}{T_1} = \frac{E}{R} \frac{\Delta T}{T_1 T_2} \tag{14}$$

where $\Delta T = T_2 - T_1$.

Eq. (14) could be used, according to Dollimore et al. [17], for determining the value of E at the midpoint of ΔT as

$$E = \frac{m(\ln T_2 - \ln T_1) R T_1 T_2}{\Delta T} \tag{15}$$

It has been proposed in [16–19] that Eq. (15) can also be used to detect changes in E and note its dependence on α. The method is simply to take the value of ΔT as small increments of 2 °C and scan the entire temperature range where the reaction is to be noted. The value of E for a particular value of α, taken as the midpoint of the ΔT increment, would be calculated from Eq. (15).

However, the proposal of Dollimore et al. [17] does not seem to take into account that the term $(\ln T_2 - \ln T_1)/\Delta T$ in a short range of ΔT represent the derivative of $\ln T$ as a function T given by the expression

$$\frac{\ln T_2 - \ln T_1}{\Delta T} \cong \frac{\mathrm{d} \ln T}{\mathrm{d}T} = \frac{1}{T} \tag{16}$$

Thus, by substituting Eq. (16) into Eq. (15) after taking into account that $T_1 T_2 \cong T^2$ (provided that T_1 is very close to T_2), we get

$$E \cong mRT \tag{17}$$

where T is the temperature at the midpoint of ΔT.

The comparison of Eqs. (15) and (17) points out that the use of Eq. (15) for calculating the activation energy as a function of the conversion necessarily leads to a linear relationship between E and T independently of the fact that the activation energy would change with α or remain unchanged all over the process. Thus, Eqs. (14) and (15) cannot be used for determining the dependence of E with α because performing the kinetic analysis just from the comparison of two constant rate approaches without any connection with the general kinetic equation governing the process has not physical meaning. Moreover, if E were depending on α, a parallel dependence of m with the conversion would be also expected. Thus, there is no reason for assuming that E is changing as a function of the conversion while m remains constant. In order to check the correctness of these statements it would be interesting to demonstrate that the use of Eq. (15) necessarily leads, firstly, to an apparent dependence of E with α and, secondly, to a linear relationships between E and T, even if the activation energy remains constant all over the process.

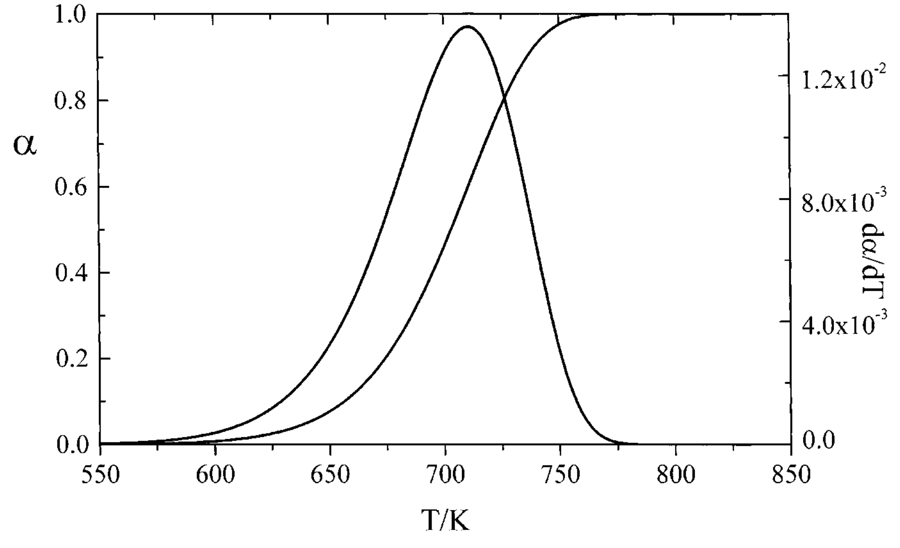

Fig. 1. TG and DTG curves simulated for a first-order reaction by assuming a heating rate $\beta = 0.01$ K s^{-1} and the following kinetic parameters: $E = 144$ kJ mol^{-1} and $A = 1.25 \times 10^7$ s^{-1}.

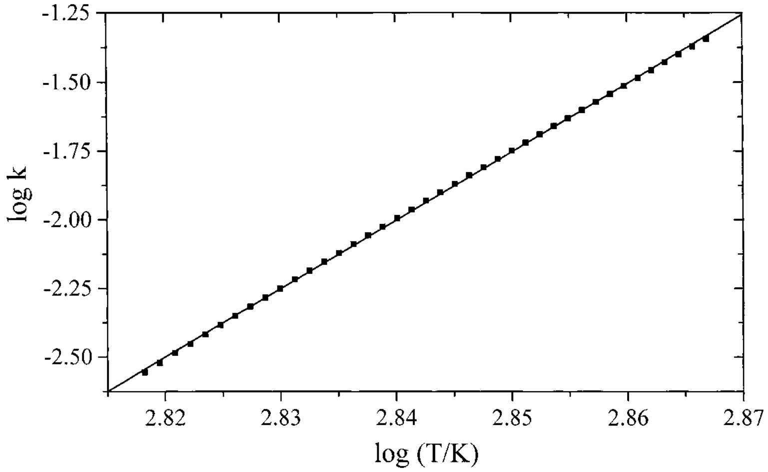

Fig. 2. Plot of the values of log k, as calculated from the data in Fig. 1, vs. log T.

3. Results

Fig. 1 shows the DTG and TG curves simulated from Eqs. (3), (5), (6) and (7) by assuming a first-order kinetic model [i.e. $f(\alpha) = (1 - \alpha)$ and $g(\alpha) = -\ln(1 - \alpha)$] and the following kinetic parameters: $E = 144$ kJ mol^{-1}, $A = 1.25 \times 10^7$ s^{-1}. A heating rate $\beta = 0.01$ K s^{-1} has been assumed. The values of log $k[k = (\mathrm{d}\alpha/\mathrm{d}t)/f(\alpha) = \beta(\mathrm{d}\alpha/\mathrm{d}T)/f(\alpha)]$ taken from Fig. 1 have been plotted in Fig. 2 as a function of the corresponding values of log T. This plot indicates a good fitting of the Harcourt and Esson relationship. Values of $m = 24.8$ and $C = 4.8 \times 10^{-73}$, with a regression coefficient $r = 0.99995$, have been obtained from the slope and intercept, respectively, of the straight line in Fig. 2.

On the other hand, the plot of the values of ln k as a function of the corresponding values of $1/T$ shown in Fig. 3 lead to a straight line whose slope and intercept, respectively, lead to an activation energy $E = 144$ kJ mol^{-1} and a preexponential factor of Arrhenius $A = 1.25 \times 10^7$ s^{-1} with a regression coefficient $r = 1$. These values are identical to those previously assumed in the whole α range for simulating the DTG

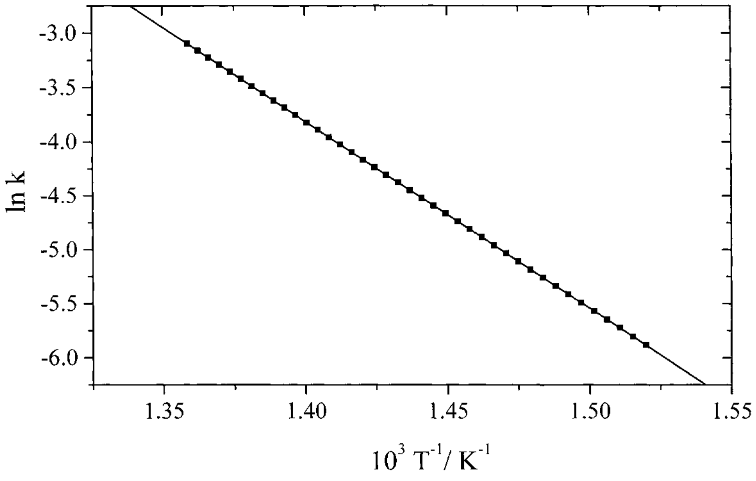

Fig. 3. Plot of the values of ln k, as calculated from the data in Fig. 1, vs. $1/T$.

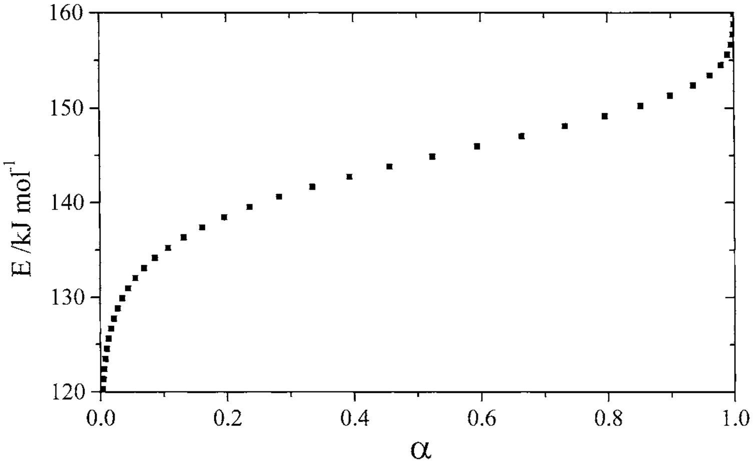

Fig. 4. Plot of E vs. α.

and TG curves included in Fig. 1. A correct kinetic analysis of the data included in Fig. 1 must lead necessarily to conclude that both the activation energy and the preexponential factor of Arrhenius are constant all over the process.

The values of E has been calculated from Eq. (15) by taking a value of ΔT as small increments of 2 °C and taking the corresponding T_1 and T_2 values by scanning the whole TG or DTG curves shown in Fig. 1. The values of E obtained in this way have been plotted in Figs. 4 and 5 versus the corresponding values of α and T, respectively, taken from the midpoint of the ΔT increment in each case. These results clearly show that Eq. (15) leads to an apparent dependence of E with T and α even if the truly activation energy of the reaction does not change. It is worth noting to point out that the linear relationship between E and T forecasted by Eq. (16) has been found. Moreover, the value $mR = 0.207\ \mathrm{kJ\ mol^{-1}\ K^{-1}}$, as calculated from the value of $m = 24.8$ previously reported, is identical to the value of the slope of the plot of E versus T shown in Fig. 5, what corroborates the validity of Eq. (17). It is noteworthy to point out that similar results have been obtained by us whatever would be the kinetic

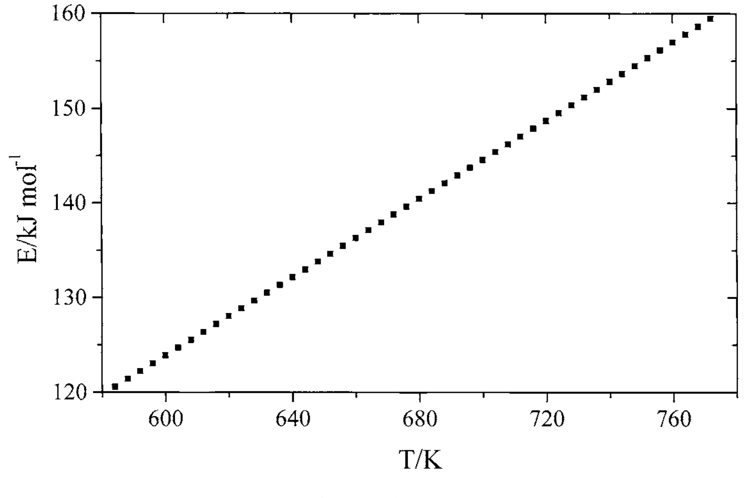

Fig. 5. Plot of E vs. T.

model or the kinetic parameters used for simulating the non-isothermal TG–DTG curves, but they have not been included for the sake of the brevity. The analysis here reported explains the linear relationship found in previous papers [16–19] between the *E* parameter determined from Eq. (15) and *T*.

4. Conclusions

The above results allow to conclude that Eq. (15) is not correct and cannot be used for determining the activation energy of solid state reactions and, therefore, it does not permit to determine the dependence of *E* with α from a single TG or DTG experiment. This is because this equation is a consequence of a mathematical artifact that imply to equalize the two approaches of the constant rate *k* expressed by the Arrhenius and the Harcourt and Esson relationships what leads to the dependence of *E* with $\Delta \ln T/\Delta T$ expressed by Eq. (15). The term $\Delta \ln T/\Delta T$ has the mathematical property of being linearly correlated with $1/T$ independently of the ΔT range considered. This means that, if the method proposed by Dollimore et al. is used for determining the activation energy, a linear relationship between *E* and *T* would be necessarily found independently of the relationship of the activation energy with α. This conclusion has been confirmed by using this method for the kinetic analysis of a DTG curve simulated for a reaction with constant activation energy in the whole α range.

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