The incorrectness of the temperature criterion

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Abstract

The errors in the activation energy of solid-state reactions calculated using "temperature criterion" method have been calculated; errors in the kinetic parameters are strongly dependent on the kinetic law obeyed by the reaction. A theoretical explanation of this behaviour is given.

Keywords: Kinetic parameters; Temperature integral; Temperature criterion; Thermal decomposition; Thermogravimetry

1. Introduction

Several attempts have been made to determine the kinetic constant of a solid-state reaction from one non-isothermal trace. In a recent work A. Mianowski and T. Radko [1] employed the "temperature criterion" developed by Szarawara and Kozik [2, 3] to estimate the approximate activation energy of solid-state processes by means of a single TG curve.

It has been prooved previously [4, 5] that the actual kinetics of a solid-state reaction cannot be discerned by means of the kinetic analysis of a single thermogravimetric curve. Moreover, it has been pointed out that any theoretical TG curve calculated using a linear heating programme by assuming a particular kinetic law does necessarily fit all the kinetic equations developed for describing solid-state reactions, although the activation energy obtained is strongly dependent on the kinetic law assumed in performing the calculations. By way of example Fig. 1 shows that a **unique** TG curve can be calculated by assuming three different kinetic models: a three-dimensional diffusion law (D3), an Avrami–Erofeev model (A2) and a random nucleation unimolecular decay law (F1).
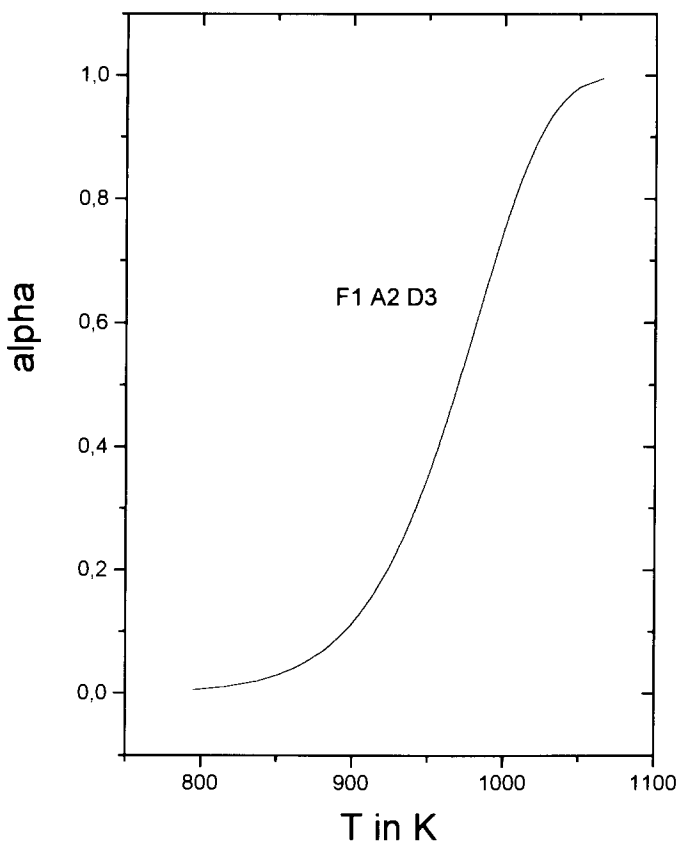
Fig. 1. A single TG curve for three different kinetic models: F1 ($E = 167$ kJ mol^{-1}, $A = 1.6 \times 10^6$ s^{-1}); A2 ($E = 76$, $A = 12$) and D3 ($E = 308$, $A = 6 \times 10^{12}$).

The aim of this paper is to prove that the "temperature criterion" method leads to very large errors in the determination of the kinetic constants of solid-state reactions and cannot, therefore, be used for any kinetic studies.

2. Theoretical

In order to calculate the error in the activation energy, E, determined using the "temperature criterion", mathematical analysis of this method is necessary. The general equation describing the reaction rate under non-isothermal conditions is given by the expression:

$$\frac{d\alpha}{dt} = A f(\alpha) \exp(-E/RT) \tag{1}$$

where α is the fraction reacted at time t and the other parameters have their usual meanings. If the TG curve is recorded at a linear heating rate β, the integration of Eq. (1) leads to:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{dt} = \frac{AE}{\beta R} p(x) \tag{2}$$

where $x = E/RT$ and $g(\alpha)$ and $f(\alpha)$ are functions depending on the actual kinetic law. Taking logarithms, Eq. (2) becomes:

$$\ln g(\alpha) = \ln \frac{AE}{\beta R} + \ln p(x) \tag{3}$$

Although it is well known [6, 7] that the function $p(x)$ cannot be expressed in a closed form, there exist several approximations with high degrees of accuracy; one of the most popular and simple is that of Doyle [8]:

$$\ln p(x) = -2.315 - 0.4567 x \tag{4}$$

It has previously been shown [9] that the accuracy of Eq. (4) is better than 10% for $E/RT > 10$. By substituting Eq. (4) into Eq. (3) it becomes:

$$\ln g(\alpha) = \ln \frac{AE}{\beta R} - 5.33 - 1.05 \frac{E}{RT} \tag{5}$$

The plot of the left-hand side of Eq. (5) as a function of the reciprocal of the temperature leads to a straight line the slope of which yields the activation energy of the process, provided that the proper $g(\alpha)$ function has been selected.

Table 1
Values of a, calculated from Eq. (7), and of the percentage error, ε, in the activation of energy for the most common mechanism operating in solid-state reactions

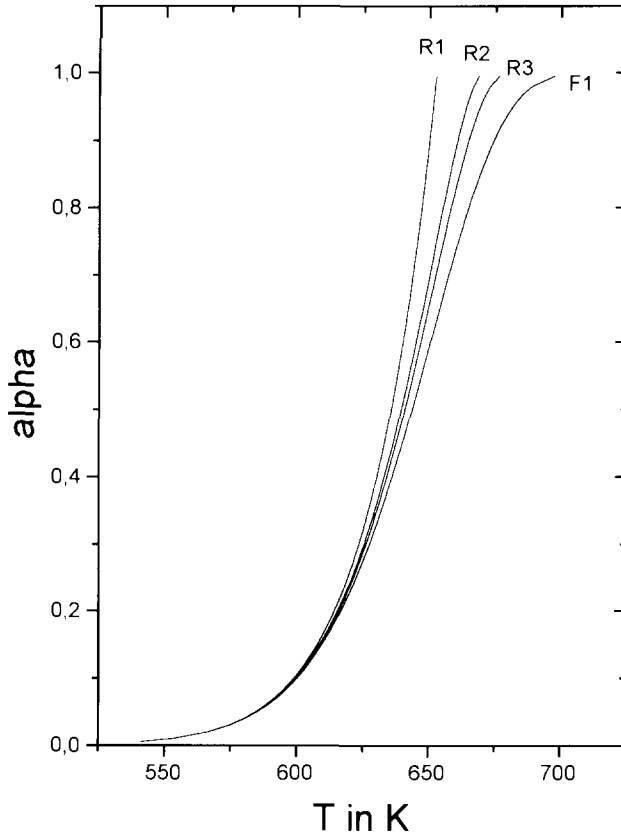| Symbol	$f(\alpha)$	$g(\alpha)$	ε in %	a	r
F1	$(1-\alpha)$	$-\ln(1-\alpha)$	1.94	1.03	0.9999
R1	1	α	5.00	1.00	0.9999
R2	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$	2.94	1.02	0.9999
R3	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$	2.94	1.02	0.9999
A2	$2[-\ln(1-\alpha)]^{1/2}(1-\alpha)$	$[-\ln(1-\alpha)]^{1/2}$	102.10	0.52	0.9999
A3	$3[-\ln(1-\alpha)]^{2/3}(1-\alpha)$	$[-\ln(1-\alpha)]^{1/3}$	200.20	0.35	0.9999
D1	$\alpha/2$	α^2	-47.50	2.01	0.9999
D2	$\dfrac{-1}{\ln(1-\alpha)}$	$(1-\alpha)\ln(1-\alpha)+\alpha$	-48.10	2.02	0.9999
D3	$\dfrac{3(1-\alpha)^{2/3}}{2[1-(1-\alpha)^{-1/3}]}$	$[1-(1-\alpha)^{1/3}]^2$	-48.50	2.04	0.9999
D4	$\dfrac{3}{2[(1-\alpha)^{-1/3}-1]}$	$\left(1-\dfrac{2\alpha}{3}\right)-(1-\alpha)^{2/3}$	-49.20	2.07	0.9999

Fig. 2. Theoretical TG curves corresponding to nth-order kinetic models obtained assuming $E = 130$ kJ mol^{-1}, $A = 10^8$ s^{-1} and $\beta = 6^c$ min^{-1}.

Szawara and Kozik [2, 3] introduced an approximation called the "**temperature criterion**" expressed by the equation:

$$\ln \alpha \cong -\frac{E}{RT} + C \quad (0 < \alpha \le 0.2) \tag{6}$$

for estimation of the approximate activation energy of a process without prior knowledge of the kinetic law.

If the following relationship can be established:

$$\ln g(\alpha) = a \ln \alpha + b \tag{7}$$

(a and b being constants) then from Eq. (5) we get:
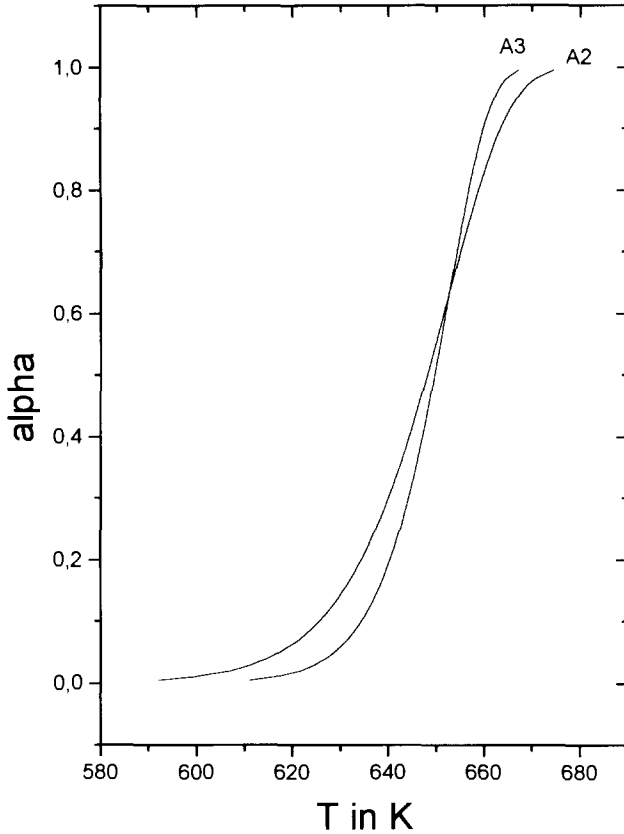
$$\ln \alpha = -\frac{1.05E}{aRT} + C \tag{8}$$

Fig. 3. Theoretical TG curves corresponding to Avrami–Erofeev kinetic models obtained assuming the same kinetic parameters as in Fig. 2.

where C is

$$C = \frac{1}{a}\ln\frac{AE}{\beta R} - \frac{5.33 - b}{a} \tag{9}$$

From comparison of Eqs. (6) and (8) it can be seen that if Eq. (7) applies then the slope of the straight line obtained from the plot of $\ln\alpha$ against $1/T$ must give an apparent activation energy $E' = 1.05E/a$. The percentage error in the activation energy calculated from the "temperature criterion" (Eq. (6)) can therefore be expressed as:

$$\varepsilon = \frac{E' - E}{E} \times 100 = \left(\frac{1.05}{a} - 1\right) \times 100 \tag{10}$$
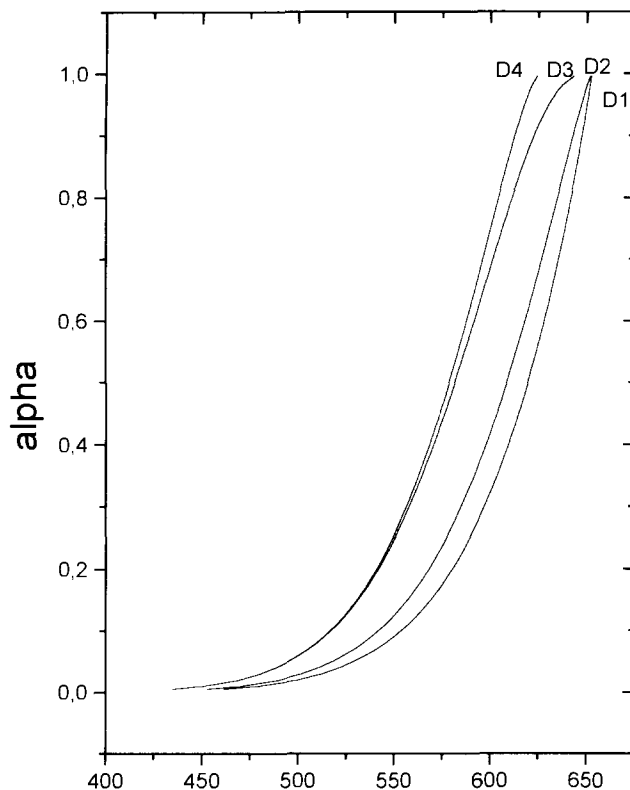
Fig. 4. Theoretical TG curves corresponding to diffusion kinetic models obtained assuming the same kinetic parameters as in Fig. 2.

In order to see if the above assumptions are valid we have collected in Table 1 the mathematical expression of the functions $f(\alpha)$ and $g(\alpha)$ corresponding to the most common kinetic laws of solid-state reactions, and we have used Eq. (7) to obtain the corresponding values of a and ε.

The values in Table 1 show that Eq. (7) holds in the range $0 < \alpha \leq 0.2$ whatever the reaction mechanism used in the literature for kinetic analysis of solid-state processes with the "temperature criterion" method. Moreover the values of ε in Table 1 reveal that the errors involved in the activation energy determined by this method are much higher than assumed in Ref. [2].

In order to check the above conclusions, in Figs. 2, 3 and 4 we have constructed the theoretical TG curves for the three kinetic families of Table 1: n-order reactions (F1, R1, R2 and R3); Avrami–Erofeev mechanisms (A2 and A3); and diffusion laws (D1, D2, D3 and D4) by assuming the following kinetic parameters $E = 130\,\text{kJ}$ mol^{-1} $A = 10^8\,\text{s}^{-1}$ and a heating rate $\beta = 6°\,\text{min}^{-1}$. The Arrhenius equation has been

Table 2
Values of the activation energies, E and E', calculated from Eqs. (5) and (6), respectively, together with the percentage error, ε, in the activation energy E', from the kinetic analysis of Figs. 2, 3 and 4

Symbol	E in kJ mol^{-1}	E'_{in} kJ mol^{-1}	ε_{in}%
F1	134.2	135.2	4.0
R1	136.3	139.3	7.1
R2	135.3	137.3	5.6
R3	134.6	136.6	5.1
A2	134.1	272.1	109.2
A3	136.2	408.2	214.1
D1	134.2	69.2	-46.8
D2	135.3	68.5	-47.3
D3	134.8	67.6	-48.0
D4	135.1	68.1	-47.6

integrated by means of the 4th degree rational approximation proposed by Senum and Yang [10].

$$\int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{E\exp(-x)(x^3 + 18x^2 + 88x + 96)}{Rx(x^4 + 20x^3 + 120x^2 + 240x + 120)} \tag{11}$$

where $x = E/RT$
which involves an error lower than 10^{-3}%.

The activation energies calculated from analysis of the kinetic data of Figs. 2, 3 and 4 by means of Eq. (5) and the "temperature criterion" (Eq. (6)) are given in Table 2. These results show the excellent agreement between the values of E determined from Eq. (5) and those previously assumed for calculating the corresponding TG curves. On the other hand, good agreement is also obtained between the values of the errors ε in E' obtained with the "temperature criterion" method and those calculated in Table 1.

3. Experimental

The TG curves of the thermal decomposition of dolomite and $Ni(NO_3)_2$ have been analyzed in order to obtain additional experimental evidence.

The dolomite sample used was supplied by S.A.E. (Productos Dolomíticos, Spain). Its analysis by atomic absorption spectrophotometry gave the following results: MgO, 21.05% (21.70); CaO, 30.20% (30.50); Al_2O_3 and Fe_2O_3, 63%; loss on ignition, 46.44% (47.72) (the figures in parentheses are the theoretical values for dolomite).

Panreac A.R. $Ni(NO_3)_2 \cdot 6H_2O$ was used to study the kinetics of the thermal decomposition of anhydrous nickel nitrate; the hydrated sample was heated in the electrobalance crucible for 2 h at 150°C under vacuum (10^{-4} mbar) before recording the TG curve.

All experiments were performed under a vacuum of 10^{-4} mbar. Thus dolomite sample was sieved between 53 and 100 μm. It was concluded in previous work [11] that under these experimental conditions the thermal decomposition of dolomite follows
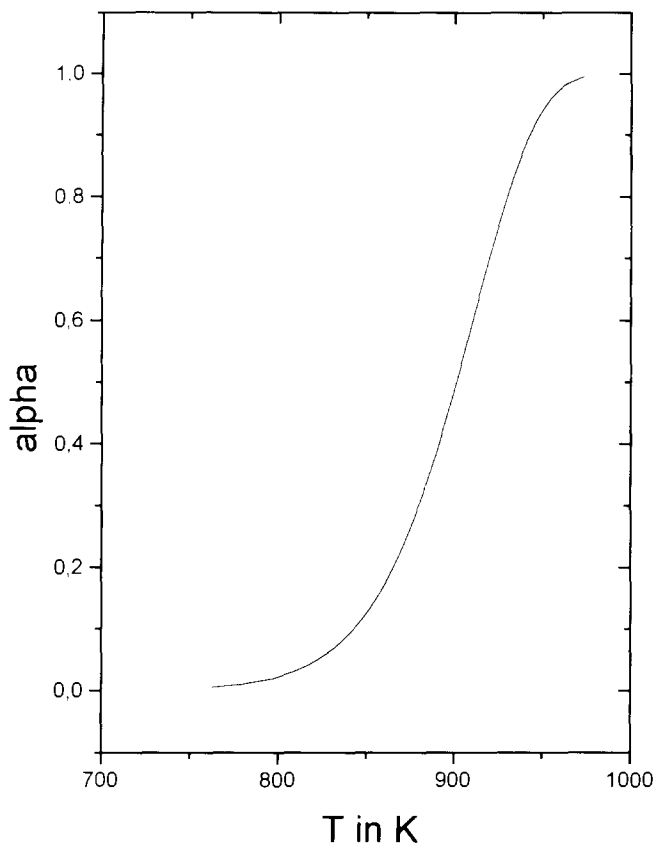
Fig. 5. Experimental TG curve for the thermal decomposition of dolomite ($\beta = 5.6°$ min^{-1}).

Table 3
Kinetic analysis of data of Figs. 5 and 6, from Eqs. (5) and (6), together with the percentage error, ε, of the "temperature criterion" method

Sample	Eq. (6)			Eq. (5)	
	E' in kJ mol^{-1}	r	ε in %	E in kJ mol^{-1}	r
Dolomite	194	0.9999	2.1	190	0.9998
$Ni(NO_3)_2$	176	0.9999	109.1	84	0.9999

a first order (F1) kinetic law. The activation energy obtained from kinetic analysis of the TG data in Fig. 5 by means of Eq. (5), after assuming the above kinetic model, is included in Table 3, together with the values of E' obtained from "temperature criterion" method with Eq. (6).
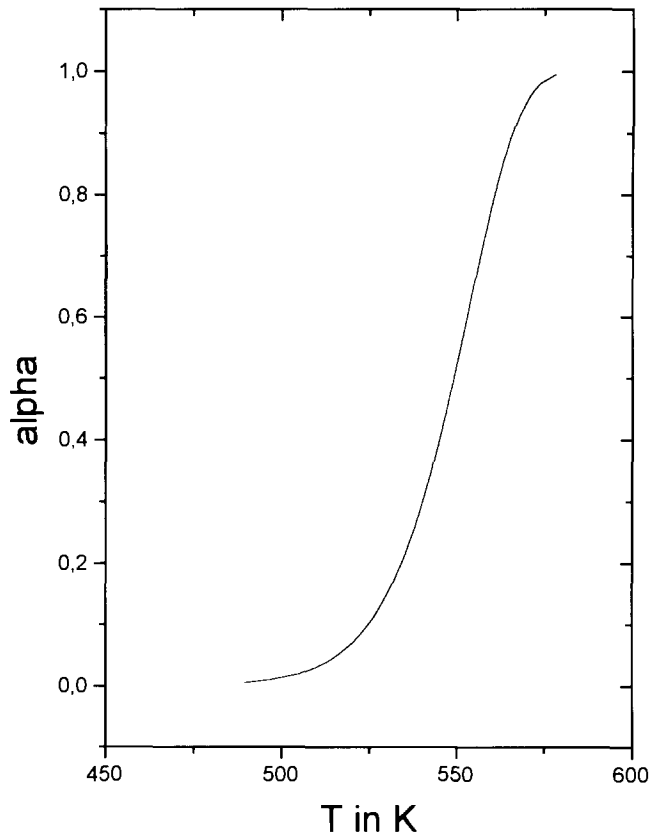
Fig. 6. Experimental TG curve for the thermal decomposition of $Ni(NO_3)_2$ ($\beta = 4°$ min^1).

It was concluded in previous work [12] that the decomposition of $Ni(NO_3)_2$ obeys on Avrami–Erofeev kinetic model, labelled A2 in Table 1. The activation energy obtained from the TG data of Fig. 6 by means of Eq. (5) is also included in Table 3 together with the values of E'. It can be seen that in both cases the values of ε are in good agreement with those calculated in Table 1.

It can be concluded that the "temperature criterion" developed by Szarawara and Kozik [2] leads to very large errors in the determination of the activation energy of solid-state reactions, the only exception being n-order processes. Therefore it cannot be used for the kinetic analysis of these reactions.

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