Kinetic analysis of thermogravimetric data obtained under linear temperature programming—a method based on calculations of the temperature integral by interpolation[☆]

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Abstract

A new technique, called interpolation method, with general application in the kinetic analysis of processes studied by thermogravimetry (TG) under linear temperature programming is developed. It is based on the linear relationship, with slope 1, between log $g(\alpha)$ and log $I(\gamma, \theta)$ for the appropriate kinetic function, where $I(\gamma, \theta)$ is the normalized temperature integral, θ the normalized temperature ($\theta = T/T_0$) and γ a dimensionless activation energy ($\gamma = E/RT_0$). Values of log $I(\gamma, \theta)$ are calculated by linear interpolations in a pre-built table. This method can easily be programmed and implemented in a personal computer, where the results (kinetic parameters and quality of regressions for the kinetic functions considered) are typically obtained in a very short time. The method is validated by analyzing different simulated thermogravimetric curves and comparing the results with those determined with some classic methods taken from the literature. In addition, the results are compared with the values obtained by a similar method, also developed and explained in this paper, which involves the evaluation of all the values of the temperature integral by numerical integration, therefore, demanding a much larger calculation time. The interpolation method is found to be more accurate than other published methods, particularly in the case of thermogravimetric curves corresponding to processes with low activation energies. The results obtained are always similar to those determined by the integration method, which is taken as reference. Application of the technique to experimental data for various types of reactions shows that the results are in agreement with the published parameters and kinetic laws. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Thermogravimetry (TG) is a convenient technique for studying the kinetics of processes involving solids, such as decomposition and gas–solid reactions, by following the weight loss and/or the rate of weight loss (DTG) of the samples with time.

There are two alternative experimental methods. In isothermal TG the solid reactant is kept under

Nomenclature

A	Arrhenius pre-exponential constant
b	heating rate
E	activation energy
k	rate constant
R	gas constant
t	time
T	temperature
u	dimensionless variable (E/RT or γ/θ)
W	weight

Greek letters

α	degree of transformation
β	dimensionless parameter (AT_0/b)
γ	dimensionless parameter (E/RT_0)
θ	normalized temperature (T/T_0)

Subscripts

0	refers to starting conditions of temperature or weight
∞	refers to residual amounts

isothermal conditions and several experiments must be carried out at different temperatures in order to determine the temperature dependency of the reaction rate. In non-isothermal TG the solid is submitted to a gradual increase in temperature (usually linear with time) and in this case it is possible, in principle, to obtain the kinetic parameters (activation energy and pre-exponential constant) and the kinetic function with a single experiment. Non-isothermal TG allows for a wide range of temperatures to be covered, which it is not always possible in isothermal TG, particularly at high temperatures, since significant solid conversion may occur during temperature stabilization at the beginning of the experiments [1]. On the other hand, one of the problems associated with rising temperature experiments is that the kinetic parameters obtained are frequently dependent on some procedural factors (heating rate, initial amount of solid sample, gas phase composition, reactor geometry, particle size, solid porosity) [2–12]. However, this situation also arises in isothermal studies [2,6,10]. The main reason for such experimental observations is certainly related to the complexity of the reaction mechanisms in the solid state [1,13,14] and the lack of mechanistic equations

accounting in full for the processes involved. Moreover, the influence of the gas phase and the problems associated with heat and mass transfer limitations [4,5,11,15] are frequently underestimated.

In the context of non-isothermal studies, the utilization of multi-heating rate data for the determination of reaction kinetics was recently recommended [1,13,14,16,17]. Apart from that, to avoid the problems of heat and mass transfer resistances, small samples of solid material (at the expense of a possible decrease in homogeneity), low particle sizes and moderate heating rates must be used [4,13,15].

According to some authors, to overcome the difficulties related to the complex nature of the mechanisms of reactions involving solids, only model-free approaches such as the so called isoconversional methods must be considered for the kinetic analysis of data [14,18,19]. However, such methods seem to be very sensitive to experimental errors [1] and the model-fitting methods continue to be extensively used for that purpose.

In this paper, a new method for kinetic analysis of thermogravimetric data obtained under linear temperature programming is developed and discussed. The technique involves the calculation of the temperature integral (actually, its logarithm) by suitable interpolations from a pre-built table of values. In the proposed procedure, the kinetic functions usually considered in this type of studies are analyzed in a systematic way. The results (kinetic function and Arrhenius parameters) are compared with those obtained either by a similar method based on the numerical integration of the temperature integral, or by application of some conventional methods. For the validation of the proposed methodology, both simulated and experimental curves from the literature are considered.

2. Theoretical considerations

2.1. Brief review of integral methods for kinetic analysis in non-isothermal thermogravimetry

The rate of decomposition of a solid depends upon the temperature and the amount of material. If only a single reaction is involved, it is usually assumed that these functions are separable and the equation used to

describe the progress of reaction is

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

where t is the time, T the absolute temperature and α the degree of transformation defined as $\alpha = \frac{(W_0 - W)}{(W_0 - W_\infty)}$, where W is the weight of solid and the subscripts 0 and ∞ refer to the initial and residual amounts, respectively.

The kinetic function $f(\alpha)$ is related to the reaction mechanism, although some authors prefer to consider empirical kinetic laws of the type $f(\alpha) = (1 - \alpha)^n$, where n is a reaction order. All functions covered in this work are listed in Table 1 [20–23], where the symbols presented are the usual ones, except for those labeled D5 and D6, which are not usually included in this type of studies.

The rate constant is normally expressed by the Arrhenius equation

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

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

Therefore,

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{3}$$

When the reaction is carried out under a linear temperature programme ($T = T_0 + bt$, where b is the heating rate and T_0 the starting temperature), Eq. (3) may be written as

$$\frac{d\alpha}{dT} = \frac{A}{b} \exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{4}$$

By separation of variables and integration, we get

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{b} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \tag{5}$$

The expressions of $g(\alpha)$ corresponding to each one of the mechanisms considered are also shown in Table 1.

On the basis of Eq. (5), it is possible to analyze experimental data by the integral method, in order to determine the kinetic function and the kinetic parameters E and A. However, the integral in the right-hand side has no exact analytical solution and several kinds of approximations are generally used. In all of them it is considered that the value of the integral between 0 and

Table 1
Algebraic expressions of $f(\alpha)$ and $g(\alpha)$ for the kinetic models considered in this work

Kinetic model	$f(\alpha)$	$g(\alpha)$	Observations
F0, R1, P1	1	α	Zero-order kinetics; one-dimensional advance of the reaction interface; power law ($\alpha = Kt$)
F1/2, R2	$(1-\alpha)^{1/2}$	$2[1 - (1-\alpha)^{1/2}]$	One-half order kinetics; two-dimensional advance of the reaction interface
F2/3, R3	$(1-\alpha)^{2/3}$	$3[1 - (1-\alpha)^{1/3}]$	Two-thirds order kinetics; three-dimensional advance of the reaction interface
F1	$(1-\alpha)$	$-\ln(1-\alpha)$	First-order kinetics
F3/2	$(1-\alpha)^{3/2}$	$2[(1-\alpha)^{-1/2} - 1]$	Three-halves order kinetics
F2	$(1-\alpha)^2$	$\alpha/(1-\alpha)$	Second-order kinetics
P2	$\alpha^{1/2}$	$2\alpha^{1/2}$	Power law ($\alpha = Kt^2$)
P3	$\alpha^{2/3}$	$3\alpha^{1/3}$	Power law ($\alpha = Kt^3$)
P4	$\alpha^{3/4}$	$4\alpha^{1/4}$	Power law ($\alpha = Kt^4$)
A2	$(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$2[-\ln(1-\alpha)]^{1/2}$	Avrami–Yerofeyev equation ($n = 2$)
A3	$(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$3[-\ln(1-\alpha)]^{1/3}$	Avrami–Yerofeyev equation ($n = 3$)
A4	$(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$4[-\ln(1-\alpha)]^{1/4}$	Avrami–Yerofeyev equation ($n = 4$)
D1	$1/\alpha$	$\alpha^2/2$	Parabolic law ($\alpha = Kt^{1/2}$)
D2	$1/-\ln(1-\alpha)$	$(1-\alpha)\ln(1-\alpha) + \alpha$	Holt–Cutler–Wadsworth equation
D3	$(1-\alpha)^{2/3}/1 - (1-\alpha)^{1/3}$	$3/2[1 - (1-\alpha)^{1/3}]^2$	Jander equation
D4	$(1-\alpha)^{1/3}/1 - (1-\alpha)^{1/3}$	$3/2[1 - 2\alpha/3 - (1-\alpha)^{2/3}]$	Ginstling–Brounshtein equation
D5	$(1-\alpha)^{5/3}/1 - (1-\alpha)^{1/3}$	$3/2[(1-\alpha)^{-1/3} - 1]^2$	Zhuravlev–Lesokhin–Tempelman equation
D6	$(1+\alpha)^{2/3}/(1+\alpha)^{1/3} - 1$	$3/2[(1+\alpha)^{1/3} - 1]^2$	Komatsu–Uemura equation (or anti-Jander equation)

T_0 is negligible, which is an acceptable hypothesis, since the starting temperature is near room temperature and the activation energy is not too low. In this case

$$g(\alpha) = \frac{A}{b} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \qquad (6)$$

This integral is called the temperature integral, which can be approximated in different ways.

The most common of them lead to expressions of the type

$$g(\alpha) = \frac{AR}{bE} T^2 Q\left(\frac{E}{RT}\right) \exp\left(-\frac{E}{RT}\right) \qquad (7)$$

where $Q(E/RT)$ is a function whose value is as closer to unity as higher is E/RT and has several particular forms, depending on the technique of approximation [24–32]. The kinetic analysis is performed through an iterative method, starting with $Q(E/RT) = 1$, on the basis of the linear equation

$$\ln \frac{g(\alpha)}{T^2 Q(E/RT)} = \ln \frac{AR}{bE} - \frac{E}{RT} \qquad (8)$$

A second type of methods is based on the fact that Eq. (6) can be written in the form

$$g(\alpha) = \frac{AE}{bR} \int_u^\infty \frac{\exp(-u)}{u^2} du = \frac{AE}{bR} p(u) \qquad (9)$$

where $u = E/RT$. In the literature, some empirical approximations of the function $p(u)$ can be found [33–36], which are valid inside well-defined intervals.

Finally, Gyulai and Greenhow [37] correlated directly the temperature integral (Eq. (6)) with the values of T and E. These authors arrived at two different expressions, with a reasonable degree of approximation in the range of temperatures 400–900 K and for activation energies between 30 and 90 kcal/mol.

It is outside of the scope of this work to discuss the relative merits of the various approximations of the temperature integral, although it can be asserted that those of Senum and Yang [27], based on polynomial expressions with degrees three or four, are very good [38] and that, generally, all of them are not good enough for low values of E/RT.

2.2. Description of the proposed method

Eq. (4) may be rendered dimensionless by normalizing the temperatures by the starting temperature and defining a new variable $\theta = T/T_0$ [39]. Then

$$\frac{d\alpha}{d\theta} = \beta \exp\left(-\frac{\gamma}{\theta}\right) f(\alpha) \qquad (10)$$

where $\beta = AT_0/b$ and $\gamma = E/RT_0$.

After separation of variables and integration, it comes

$$g(\alpha) = \beta I(\gamma, \theta) \qquad (11)$$

where

$$I(\gamma, \theta) = \int_1^\theta \exp\left(-\frac{\gamma}{\theta}\right) d\theta \qquad (12)$$

Eq. (11) is structurally similar to Eq. (5), but has the advantage of setting the lower value of the integration interval without doing any simplification (as $T_0 = 0$). The integral presented in Eq. (12) depends only on two dimensionless quantities (the parameter γ, which contains the activation energy, and the normalized variable θ), while the integral in the right-hand side of Eq. (5) depends on T_0 (defined by the experimental conditions), the activation energy and the variable T. So, the method proposed in this work is based on the use of normalized temperatures, although it can be extended to Eq. (5), with additional complications.

Eq. (11) can be linearized by application of decimal logarithms to both sides, leading to

$$-\log g(\alpha) = -\log \beta + [-\log I(\gamma, \theta)] \qquad (13)$$

The minus sign was inserted for convenience, because the integral values are generally <1 at the normalized temperatures of practical importance, with the exception of some cases corresponding to extremely low γ values ($\gamma < 4$).

According to Eq. (13), a linear relationship with slope 1 must be obtained when $[-\log g(\alpha)]$ is plotted versus $[-\log I(\gamma, \theta)]$, for the correct kinetic law and the γ value associated to the reaction. So, in the method proposed here, starting from a normalized thermogravimetric curve α versus θ obtained under linear temperature programming, the values of the parameter γ that originate such slope are successively determined for all the kinetic functions listed in Table 1. At the end of this analysis, the choice of the most satisfactory kinetic function is performed on the basis of the linear regression quality. The kinetic parameter β is calculated from the intercept of the fitted straight line.

The strategy used to calculate the values of $[-\log I(\gamma, \theta)]$ and the methodology followed to make the approach to the solution, in other words, to the γ value that originates a slope equal to 1, remain to be explained.

Initially, a table of values of $(-\log I)$ is built as a function of γ and θ. The integral $I(\gamma, \theta)$ (Eq. (12)) can be determined numerically, for instance, by the Simpson rule, establishing a low enough allowed maximum error, according to the desired objectives (we considered at least seven significant figures in our calculations). Besides, our table was calculated for θ values between 1.1 and 5.0 (increments of 0.1) and for γ values in the range 0–500 (increments of 5). These limits largely exceed the values usually found in real reactions.

Next, the values of $(-\log I)$ corresponding to the normalized temperatures considered in the α versus θ curve which is the object of analysis are calculated by linear interpolation relatively to $1/\theta$ for all the values of γ presented in the original table, above mentioned. According to the different types of approximations of the temperature integral, discussed in Section 2.1 (see for instance Doyle's expression of log $p(u)$ [33]), this procedure may be expected to lead to better results than performing linear interpolations relatively to θ. Observation of Table 2, where some calculated values of $(-\log I)$ are shown as well as the errors that correspond to the two interpolation procedures, confirms this assumption. As a matter of fact, not only the errors associated to the interpolation relatively to $1/\theta$ are generally much smaller, but it can also be confirmed that they are negligible, with the exception of those corresponding to low γ and θ values, although they are still admissible in these cases.

In order to find the value of the parameter γ for each of the kinetic functions, the interval with magnitude $\Delta\gamma = 5$ within which the slope of the straight line defined by Eq. (13) is equal to 1 is determined in the first place. This is done by systematic search directly on the table of $(-\log I)$ values obtained in the previous step. It is recommended to begin the determinations of the slope for γ values in large intervals (for instance, of 50) and, after that, for increments of 5 inside the previously defined interval. After determination of the interval with $\Delta\gamma = 5$ mentioned above, the solution is calculated by the bisection method. For each value of γ that appears during this procedure, the

Table 2

Numerically calculated values of $(-\log I)$ and absolute errors associated with their determination by linear interpolation relatively to θ and $1/\theta$

γ	θ	$-\log I$	Error[a]	Error[b]
0	1.15	0.8239087	2.56×10^{-2}	1.90×10^{-2}
	1.25	0.6020600	8.86×10^{-3}	5.34×10^{-3}
	1.55	0.2596373	1.80×10^{-3}	5.25×10^{-4}
	2.55	−0.1903317	2.26×10^{-4}	-4.87×10^{-5}
	3.55	−0.4065402	8.35×10^{-5}	-3.64×10^{-5}
	4.95	−0.5965971	3.48×10^{-5}	-2.07×10^{-5}
50	1.15	20.4795573	3.81×10^{-2}	6.01×10^{-4}
	1.25	18.8976596	2.86×10^{-2}	-6.41×10^{-4}
	1.55	15.3532276	1.50×10^{-2}	-4.28×10^{-4}
	2.55	9.4419258	3.44×10^{-3}	-1.54×10^{-4}
	3.55	6.7699547	1.30×10^{-3}	-7.75×10^{-5}
	4.95	4.7697626	4.91×10^{-4}	-3.87×10^{-5}
100	1.15	39.6531108	7.24×10^{-2}	-7.85×10^{-4}
	1.25	36.5603362	5.64×10^{-2}	-6.79×10^{-4}
	1.55	29.6514032	2.96×10^{-2}	-4.39×10^{-4}
	2.55	18.2391891	6.72×10^{-3}	-1.60×10^{-4}
	3.55	13.1620793	2.51×10^{-3}	-8.13×10^{-5}
	4.95	9.4237779	9.39×10^{-4}	-4.09×10^{-5}
150	1.15	58.7083618	1.08×10^{-1}	-8.09×10^{-4}
	1.25	54.1047302	8.42×10^{-2}	-6.84×10^{-4}
	1.55	43.8327227	4.42×10^{-2}	-4.43×10^{-4}
	2.55	26.9240380	9.99×10^{-3}	-1.62×10^{-4}
	3.55	19.4457648	3.73×10^{-3}	-8.28×10^{-5}
	4.95	13.9742885	1.39×10^{-3}	-4.19×10^{-5}

[a] Linear interpolation with respect to θ.

[b] Linear interpolation with respect to $1/\theta$.

calculation of $(-\log I)$ is done by linear interpolation. Table 3 shows that the errors are generally small and can only be significant for low γ values, which is the situation with less practical interest in the context of solid state reactions. Note that, for example, $\gamma = 10$ corresponds to an activation energy of only about 25 kJ/mol, in an experiment with linear temperature programming starting at room temperature. By application of the bisection method, subintervals of decreasing width that contain the γ value corresponding to a slope of 1 relatively to Eq. (13) are successively defined. Of course, in the two limits of those subintervals, the variable (slope−1) has opposite signs. The procedure ends according to a pre-established error. In the examples presented in this work, the stopping criterion considered is that $|\text{slope} - 1| < 5 \times 10^{-5}$. The results for all the kinetic functions analyzed (see Table 1)

Table 3
Numerically calculated values of $(-\log I)$ and absolute errors associated with their determination by linear interpolation relatively to γ

θ	γ	$-\text{Log } I$	Error
1.1	2.5	2.0338853	-9.27×10^{-4}
	7.5	4.0961175	-9.00×10^{-4}
	22.5	10.2410912	-7.41×10^{-4}
	47.5	20.3716153	-4.26×10^{-4}
	97.5	40.4101407	-1.36×10^{-4}
	147.5	60.3273326	-6.11×10^{-5}
1.5	2.5	1.1695260	-1.11×10^{-2}
	7.5	2.8430419	-7.87×10^{-3}
	22.5	7.5661457	-2.13×10^{-3}
	47.5	15.1030402	-5.38×10^{-4}
	97.5	29.8789367	-1.35×10^{-4}
	147.5	44.5308934	-6.00×10^{-5}
2.0	2.5	0.7277441	-2.20×10^{-2}
	7.5	2.0682690	-1.09×10^{-2}
	22.5	5.7025748	-2.05×10^{-3}
	47.5	11.4230149	-5.21×10^{-4}
	97.5	22.5759368	-1.32×10^{-4}
	147.5	33.6074230	-5.92×10^{-5}
3.0	2.5	0.2575805	-2.83×10^{-2}
	7.5	1.2266981	-1.08×10^{-2}
	22.5	3.7494385	-1.86×10^{-3}
	47.5	7.6479423	-4.90×10^{-4}
	97.5	15.1745752	-1.28×10^{-4}
	147.5	22.5843578	-5.78×10^{-5}
4.0	2.5	-0.0172916	-2.92×10^{-2}
	7.5	0.7525621	-9.84×10^{-3}
	22.5	2.7103289	-1.71×10^{-3}
	47.5	5.6933694	-4.64×10^{-4}
	97.5	11.4038900	-1.24×10^{-4}
	147.5	17.0016706	-5.66×10^{-5}
5.0	2.5	-0.2077479	-2.83×10^{-2}
	7.5	0.4371785	-8.92×10^{-3}
	22.5	2.0509290	-1.59×10^{-3}
	47.5	4.4817184	-4.42×10^{-4}
	97.5	9.1004705	-1.20×10^{-4}
	147.5	13.6101997	-5.54×10^{-5}

are ordered according to the determination coefficient (r^2) obtained in the last iteration.

The method just described, which is the basis of this work, is called ''interpolation method'' in the following pages. The algorithm presented can be easily programmed and implemented in a personal computer and the results are obtained in a very short time.

For comparison, another calculation method was considered-''integration method''. In this case, the

determination of γ for each kinetic function is also performed on the basis of the bisection method, but the procedure begins in the γ interval [0, 500]. Besides, all the values of the integral $I(\gamma, \theta)$ associated to the normalized temperatures considered in the thermogravimetric curve are evaluated numerically in each calculation step, using the Simpson rule. As no interpolations are involved in this method, errors of the type presented in Tables 2 and 3 do not occur, and the results have a greater accuracy. Obviously, the calculation times are much larger.

3. Results and discussion

3.1. Simulated thermogravimetric curves

A considerable number of simulated thermogravimetric curves were analyzed by the methods described in the previous section (interpolation and integration methods), considering many pairs of values of the dimensionless kinetic parameters γ and β and all the kinetic functions listed in Table 1. Among these, six representative examples are shown in Fig. 1. The points used in the analyses are also presented over the curves.

For comparison, some of the conventional methods of kinetic analysis, namely, those developed by Coats and Redfern [24], Senum and Yang [27] and Madhusudanan et al. [34], were also considered.

The first two are representative of the methodology that leads to Eqs. (7) and (8) (see Section 2.1); one of them was chosen because it is a classical and frequently used method (Coats and Redfern, CR), the other due to the high accuracy attributed to it when based on polynomial expressions with degree three and higher (Senum and Yang, SY) [38,40]. In terms of dimensionless quantities, Eq. (8) can be written in the form

$$\ln \frac{g(\alpha)}{\theta^2 Q(\gamma/\theta)} = \ln \frac{\beta}{\gamma} - \frac{\gamma}{\theta} \tag{14}$$

The kinetic parameters are obtained by an iterative procedure, starting with $Q(\gamma/\theta) = 1$. Designating $u = E/RT = \gamma/\theta$, the expressions of function Q are
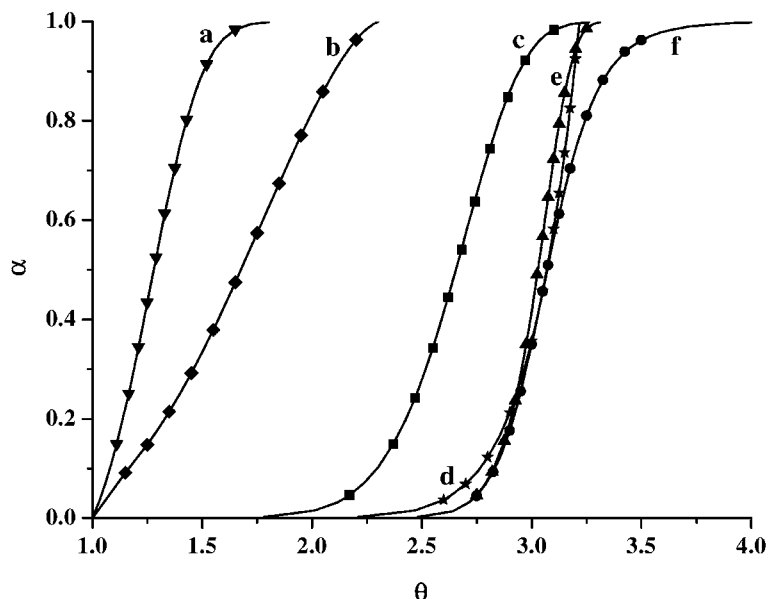
$$Q(u) = \frac{u-2}{u} \tag{15}$$

Fig. 1. Simulated thermogravimetric curves selected for kinetic analysis (a: F1/6.87/2.99; b: D4/10.00/2.00; c: F1/27.48/5.00; d: P3/10.00/2.00; e: F1/74.72/11.50; f: F2/74.72/11.50). These denominations refer to: kinetic function/γ/log β).

in the CR method and

$$Q(u) = \frac{u^3 + 10u^2 + 18u}{u^3 + 12u^2 + 36u + 24} \tag{16}$$

for the third degree approximation of SY.

On the other hand, Eq. (9) can be written in dimensionless form as

$$g(\alpha) = (\beta\gamma)p(u) \tag{17}$$

Considering the expression for $p(u)$ developed by Madhusudanan, Krishnan and Ninan (MKN) after linearization, it comes

$$\ln\frac{g(\alpha)}{\theta^{1.921503}} = \ln(\beta\gamma) - 0.297580$$
$$- 1.921503\ln\gamma - 1.000953\frac{\gamma}{\theta} \tag{18}$$

In this case, a linear relationship between the left-hand side of Eq. (18) and the variable $1/\theta$ must be found for the correct kinetic model. The parameters γ and β are obtained from the slope and the intercept, respectively. This method was selected among those of the same type, since previous studies have shown its superior quality in almost all situations.

The results obtained for the simulated curves corresponding to F2/74.72/11.50 and F1/74.72/11.50

(denominations that refer to: kinetic function/γ/log β) are shown in Tables 4 and 5, respectively. The kinetic functions are presented according to the decreasing order of the determination coefficients as calculated with the interpolation or integration methods. The results associated to the methods of CR, SY, and MKN are also shown.

In these examples, which correspond to relatively high activation energy (about 180 kJ/mol for experiments starting at room temperature) and values of u also high ($u > 20$), all the methods lead to similar kinetic parameters, for the correct kinetic functions. Actually, for the interpolation, integration and SY methods, they are exactly the same. It should be noted that these parameters are slightly different from the original ones ($\gamma = 74.72$ and $\log \beta = 11.50$), probably because values of α with just three decimal figures were considered in the analyses. For the correct kinetic functions, the methods of CR and of MKN lead to values of γ a little higher or lower, respectively. However, the corresponding small variations of $\log \beta$ make the compensation and the calculated thermogravimetric curves also approach the original points (differences in $\alpha < 0.005$).

The decreasing order of the determination coefficients, which represents an increasingly significant

Table 4
Results of the kinetic analysis corresponding to the TG curve for F2/74.72/11.50

Kinetic function	Interpolation			Integration			CR			SY			MKN		
	γ	Log β	r^2	γ	Log β	r^2	γ	Log β	r^2	γ	Log β	r^2	γ	Log β	r^2
F2	74.74	11.50	1.000	74.74	11.50	1.000	74.80	11.52	1.000	74.74	11.50	1.000	74.68	11.49	1.000
F3/2	60.56	9.28	0.992	60.56	9.28	0.992	60.66	9.30	0.991	60.58	9.28	0.991	60.49	9.26	0.991
D5	118.45	16.74	0.986	118.45	16.74	0.986	118.50	16.75	0.985	118.47	16.74	0.985	118.45	16.74	0.985
F1	48.68	7.39	0.966	48.68	7.39	0.966	48.85	7.42	0.958	48.71	7.39	0.958	48.59	7.37	0.958
A2	21.66	3.69	0.965	21.65	3.69	0.965	22.30	3.84	0.950	21.69	3.70	0.946	21.32	3.61	0.944
A3	12.81	2.48	0.964	12.80	2.48	0.964	14.37	2.85	0.949	12.83	2.49	0.931	12.23	2.32	0.923
A4	8.48	1.89	0.963	8.46	1.89	0.963	11.29	2.56	0.961	8.51	1.90	0.911	7.69	1.63	0.889
D3	90.04	12.31	0.940	90.04	12.31	0.940	90.13	12.33	0.932	90.09	12.32	0.932	90.06	12.31	0.932
F2/3	42.16	6.34	0.939	42.16	6.34	0.939	42.39	6.39	0.923	42.21	6.35	0.922	42.05	6.31	0.922
F1/2	39.32	5.88	0.923	39.32	5.88	0.923	39.57	5.93	0.902	39.37	5.89	0.901	39.20	5.85	0.900
D4	82.21	11.08	0.917	82.20	11.08	0.917	82.31	11.10	0.906	82.26	11.08	0.906	82.22	11.08	0.906
D2	78.44	10.96	0.904	78.44	10.96	0.904	78.56	10.98	0.891	78.51	10.97	0.891	78.46	10.96	0.891
D1	70.13	9.63	0.874	70.12	9.63	0.874	70.27	9.66	0.855	70.20	9.64	0.855	70.14	9.63	0.855
F0	32.26	4.72	0.872	32.25	4.72	0.872	32.62	4.80	0.835	32.33	4.73	0.831	32.10	4.68	0.829
P2	13.59	2.30	0.869	13.58	2.30	0.869	15.04	2.64	0.814	13.65	2.31	0.775	13.07	2.15	0.758
P3	7.56	1.51	0.867	7.53	1.52	0.867	10.77	2.28	0.852	7.62	1.53	0.703	6.73	1.24	0.645
P4	4.59	1.13	0.865	4.59	1.14	0.865	–[a]	–	–	4.75	1.17	0.617	3.56	0.69	0.468
D6	63.50	8.06	0.857	63.49	8.06	0.857	63.66	8.09	0.834	63.58	8.07	0.834	63.50	8.06	0.834

[a] Not considered (negative values of $Q(u)$).

Table 5
Results of the kinetic analysis corresponding to the TG curve for F1/74.72/11.50

Kinetic function	Interpolation			Integration			CR			SY			MKN		
	γ	Log β	r^2	γ	Log β	r^2	γ	Log β	r^2	γ	Log β	r^2	γ	Log β	r^2
F1	74.77	11.51	1.000	74.77	11.51	1.000	74.82	11.52	1.000	74.77	11.51	1.000	74.72	11.50	1.000
A2	34.69	5.84	1.000	34.68	5.84	1.000	34.91	5.89	1.000	34.69	5.84	1.000	34.49	5.79	1.000
A3	21.44	3.96	1.000	21.43	3.96	1.000	21.99	4.10	1.000	21.43	3.96	1.000	21.08	3.87	1.000
A4	14.88	3.04	1.000	14.87	3.04	1.000	15.95	3.30	1.000	14.88	3.04	1.000	14.38	2.90	1.000
D3	136.15	19.45	0.994	136.15	19.45	0.994	136.18	19.45	0.993	136.17	19.45	0.993	136.14	19.45	0.993
F2/3	65.26	10.00	0.994	65.26	10.00	0.994	65.34	10.02	0.993	65.27	10.00	0.993	65.20	9.99	0.993
D5	178.03	25.93	0.993	178.02	25.93	0.993	178.03	25.93	0.993	178.02	25.93	0.993	177.98	25.93	0.993
F1/2	61.19	9.35	0.987	61.18	9.35	0.987	61.27	9.37	0.984	61.20	9.36	0.984	61.12	9.34	0.984
F3/2	92.55	14.30	0.985	92.54	14.29	0.985	92.57	14.30	0.983	92.53	14.29	0.983	92.50	14.29	0.983
D4	124.94	17.70	0.983	124.94	17.70	0.983	124.98	17.71	0.982	124.96	17.70	0.982	124.94	17.70	0.982
D2	119.63	17.35	0.976	119.63	17.35	0.976	119.67	17.35	0.974	119.65	17.35	0.974	119.63	17.35	0.974
D1	108.05	15.52	0.959	108.04	15.52	0.959	108.09	15.53	0.955	108.07	15.53	0.955	108.04	15.52	0.955
F0	51.24	7.76	0.959	51.23	7.76	0.959	51.37	7.79	0.950	51.26	7.76	0.950	51.16	7.74	0.949
P2	23.01	3.90	0.958	23.01	3.90	0.958	23.52	4.02	0.940	23.03	3.91	0.937	22.71	3.82	0.935
P3	13.75	2.63	0.957	13.73	2.64	0.957	14.99	2.94	0.936	13.76	2.64	0.922	13.23	2.49	0.915
P4	9.20	2.01	0.957	9.18	2.02	0.957	11.51	2.58	0.943	9.22	2.02	0.903	8.49	1.78	0.885
D6	98.54	13.52	0.950	98.53	13.52	0.950	98.59	13.53	0.944	98.56	13.52	0.944	98.54	13.52	0.944
F2	113.96	17.63	0.948	113.96	17.63	0.948	113.95	17.63	0.943	113.93	17.62	0.943	113.91	17.62	0.943

deviation relatively to the correct kinetic function, is not the same in all methods employed. As a matter of fact, the published methods can originate a different order (for instance, see the r^2 value for D4 function compared with that of F1/2 in Table 4 or, in Table 5, the corresponding values for D6 and F2 models relatively to those of P2, P3 and P4). These observations are directly related to the low accuracy of the temperature integral approximations associated to those methods in the low activation energy range. So, when the solution corresponds to a lower γ, there is an additional tendency to yield a worse fit. However, the opposite effect can also be observed in the application of the CR method (see A4 and P3 functions in Table 4), as if the errors of the respective approximation had a partial compensation effect for the corresponding particular values of γ.

Although the results presented in Table 5 refer to first-order kinetics, it can be observed that the A2, A3 and A4 functions also fit the simulated curve, obviously for different values of parameters γ and $\log \beta$. This situation can be understood on the basis of the respective $g(\alpha)$ expressions (see Table 1). In fact, the values of $\ln g(\alpha)$ for those kinetic models are

directly related to the corresponding values for the F1 model through

$$\ln g(\alpha)_{An} = \ln n + \frac{1}{n} \ln g(\alpha)_{F1} \tag{19}$$

As Criado and Morales [41] explained, this relationship associated with the fact that the reactions typically occur in a narrow range of temperatures, giving rise to $\ln T$ (or $\ln \theta$) values approximately constant inside that interval, make the discrimination between the mentioned models impossible or at least difficult, in the context of non-isothermal thermogravimetric experiments. The thermogravimetric curves calculated with the parameters obtained for the A2, A3 and A4 functions by the interpolation, integration and SY methods (practically independent of the method) show a good agreement with the original simulated curve. However, repeating the procedure for the kinetic parameters corresponding to the methods of CR and MKN, large differences are observed (Fig. 2), in spite of the good quality of the fits ($r^2 = 1.000$). These deviations are positive for the former method and negative for the latter. It is important to note that the mentioned differences increase from A2 to A4, in
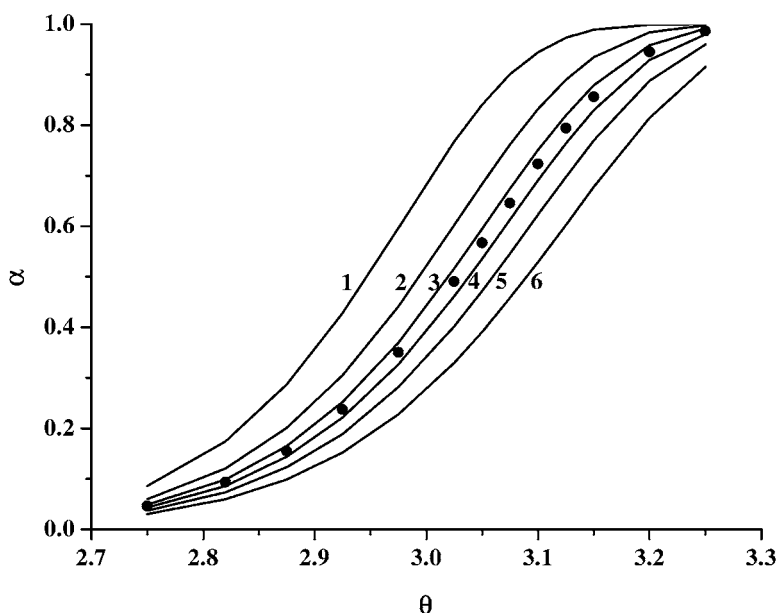

Fig. 2. Points considered in the kinetic analysis of the thermogravimetric curve corresponding to F1/74.72/11.50 and calculated curves from the results obtained by the Coats and Redfern (1, 2, 3) and the Madhusudanan, Krishnan and Ninan (4, 5, 6) methods for the mechanisms A2 (3, 4), A3 (2, 5) and A4 (1, 6).

Table 6
Results of the kinetic analysis corresponding to the TG curve for F1/27.48/5.00

Kinetic function	Interpolation			Integration			CR			SY			MKN		
	γ	Log β	r^2	γ	Log β	r^2	γ	Log β	r^2	γ	Log β	r^2	γ	Log β	r^2
F1	27.48	5.00	1.000	27.48	5.00	1.000	27.71	5.06	1.000	27.48	5.00	1.000	27.29	4.95	1.000
A2	11.64	2.48	1.000	11.63	2.48	1.000	12.77	2.80	1.000	11.63	2.49	1.000	11.16	2.33	1.000
A3	6.47	1.66	1.000	6.46	1.67	1.000	–[a]	–	–	6.52	1.68	1.000	5.79	1.39	0.999
A4	3.84	1.23	1.000	3.89	1.26	1.000	–	–	–	4.07	1.30	0.999	3.10	0.83	0.995
D3	51.83	8.12	0.994	51.82	8.12	0.994	51.91	8.15	0.993	51.84	8.13	0.993	51.78	8.11	0.993
F2/3	23.62	4.23	0.993	23.61	4.23	0.993	23.95	4.32	0.991	23.64	4.23	0.990	23.41	4.17	0.990
D5	68.90	11.39	0.992	68.89	11.39	0.992	68.91	11.39	0.991	68.87	11.38	0.991	68.84	11.38	0.991
F1/2	21.97	3.89	0.986	21.96	3.89	0.986	22.35	3.99	0.980	21.99	3.90	0.979	21.74	3.83	0.978
F3/2	34.71	6.42	0.984	34.71	6.42	0.984	34.82	6.45	0.980	34.67	6.41	0.980	34.54	6.37	0.980
D4	47.25	7.24	0.983	47.25	7.24	0.983	47.37	7.26	0.979	47.28	7.24	0.979	47.20	7.22	0.979
D2	45.08	7.29	0.975	45.08	7.29	0.975	45.21	7.32	0.969	45.12	7.30	0.969	45.03	7.28	0.969
D1	40.37	6.36	0.955	40.37	6.36	0.955	40.54	6.40	0.945	40.43	6.37	0.944	40.32	6.34	0.944
F0	17.94	3.06	0.953	17.94	3.06	0.953	18.51	3.22	0.934	17.99	3.07	0.928	17.68	2.98	0.925
P2	6.97	1.45	0.950	6.96	1.46	0.950	–	–	–	7.05	1.47	0.880	6.36	1.21	0.851
P3	3.29	0.89	0.949	3.36	0.93	0.948	–	–	–	3.62	0.98	0.805	2.58	0.46	0.656
P4	1.41	0.61	0.949	1.50	0.66	0.948	–	–	–	2.05	0.77	0.693	0.70	−0.21	0.183
F2	43.43	8.10	0.946	43.43	8.10	0.946	43.46	8.11	0.934	43.37	8.09	0.934	43.27	8.07	0.934
D6	36.59	5.10	0.943	36.59	5.10	0.943	36.79	5.14	0.929	36.65	5.11	0.929	36.53	5.07	0.928

[a] Not considered (negative values of $Q(u)$).

other words in the direction of the lower γ values. This shows clearly the lack of rigor of those methods when the activation energies are not high enough.

The results obtained in the analysis of the thermogravimetric curve corresponding to a first-order reaction with $\gamma = 27.48$ and log $\beta = 5.00$ are summarized in Table 6. It should be mentioned that it was not possible to obtain any results by the CR method for the kinetic functions that correspond to very low γ (less than about 7), since some negative $Q(u)$ values occur after the first iteration. As in the cases mentioned before, the interpolation, integration and SY methods lead to equal parameters for the correct kinetic function F1. The other two methods originate significantly different values of γ, and the corresponding variations of log β do not produce a total compensation effect. Thus, the corresponding calculated curves are slightly displaced relatively to the original points (upwards for the results of the CR method and downwards for those obtained with the MKN expression), although the differences do not exceed 0.02 in terms of α.

Since the analyzed curve corresponds to a first-order reaction, good fits are also generally obtained for the kinetic functions associated to the Avrami–Yerofeyev mechanisms. With respect to A2, the results of

the interpolation and SY methods are very similar to those of the integration method, taken as reference. For the kinetic models A3 and A4 there are some deviations, particularly evident in the second case, as a consequence of the corresponding very low γ values. The other two methods lead to very different parameters, in spite of the relatively high determination coefficients obtained, as occurs for the A2 function. On the other hand, the associated calculated curves are far away from the original points.

Considering now the results obtained for the selected points in the simulated curve corresponding to F1/6.87/2.99 (Table 7), larger differences between the determined parameters for the correct kinetic function are found, as a consequence of the low value of γ involved. The integration method leads to values that correspond to the expected ones. The small deviation in γ (6.88 instead of 6.87) certainly results from the consideration of just three decimal figures for the values of α used in the calculations. The kinetic parameters obtained with the interpolation method ($\gamma = 6.69$ and log $\beta = 2.92$) are slightly lower than the original parameters. In spite of this, the corresponding calculated curve approaches the considered points, as can be seen in Table 8. Considering the

Table 7
Results of the kinetic analysis corresponding to the TG curve for F1/6.87/2.99

Kinetic function[a]	Interpolation			Integration			CR			SY			MKN		
	γ	Log β	r^2	γ	Log β	r^2	γ	Log β	r^2	γ	Log β	r^2	γ	Log β	r^2
F1	6.69	2.92	1.000	6.88	2.99	1.000	8.74	3.66	0.994	8.42	3.49	0.992	8.24	3.38	0.992
D5	23.37	8.15	0.998	23.42	8.17	0.998	23.67	8.25	0.997	23.62	8.23	0.997	23.58	8.21	0.997
F2/3	4.43	2.01	0.996	4.60	2.07	0.996	7.12	3.00	0.967	6.61	2.73	0.957	6.39	2.58	0.952
F1/2	3.34	1.57	0.991	3.59	1.67	0.991	6.48	2.74	0.948	5.86	2.40	0.927	5.61	2.24	0.918
F3/2	10.84	4.57	0.988	10.96	4.61	0.989	12.08	5.01	0.991	11.91	4.92	0.991	11.79	4.85	0.991
D3	14.83	4.80	0.984	14.90	4.83	0.984	15.54	5.05	0.971	15.43	5.00	0.970	15.34	4.95	0.970
F0	0.81	0.53	0.973	1.05	0.62	0.971	5.18	2.19	0.890	4.11	1.61	0.799	3.79	1.38	0.765
D4	12.52	3.88	0.968	12.63	3.92	0.967	13.45	4.21	0.941	13.32	4.14	0.939	13.21	4.08	0.938
F2	15.59	6.42	0.963	15.68	6.45	0.964	16.31	6.68	0.960	16.22	6.63	0.959	16.14	6.58	0.959
D2	11.44	3.92	0.958	11.55	3.96	0.956	12.49	4.29	0.921	12.33	4.21	0.918	12.21	4.15	0.916
D1	9.15	2.98	0.936	9.27	3.03	0.934	10.51	3.47	0.875	10.29	3.35	0.867	10.14	3.27	0.863
D6	7.44	1.75	0.931	7.61	1.82	0.929	9.16	2.37	0.853	8.86	2.22	0.841	8.69	2.11	0.834

[a] The kinetic functions A2, A3, A4, P2, P3 and P4 are not considered, since both the interpolation and the integration methods originate negative γ values.

published methods studied, the associated parameters, for the correct kinetic function F1, are too high and bad fits are observed (see Tables 7 and 8). It is interesting to note that it is not possible to discriminate the true model by any of these methods. In effect, the best results are obtained for the mechanism named D5 ($r^2 = 0.997$), for which the determined parameters are similar, independently of the method. In the last column of Table 8, some values of α of the TG curve calculated with the parameters obtained by application of the SY method and corresponding to D5 are shown. A greater approximation to the original points can be observed, in comparison with the curve determined with the parameters related to the correct kinetic function F1. Therefore, if γ is small, the interpolation method, in spite of its simplicity, is better both in what concerns parameter accuracy and kinetic model discrimination. Although simple reactions with low activation energies (low γ) are not very common in the decomposition of solid materials, this conclusion is important in some situations such as the desorption of gases from solid surfaces [38]. It may be also relevant in the context of the decomposition of complex materials (for instance, coal and biomass) where lumped

Table 8
Comparison between the simulated TG curve for F1/6.87/2.99 and the curves calculated from the results obtained by application of the mentioned methods

θ	α					
	Simulated, F1/6.87/2.99	Interpolation, F1/6.69/2.92	CR, F1/8.74/3.66	SY, F1/8.42/3.49	MKN, F1/8.24/3.38	SY, D5/23.62/8.23
1.110	0.149	0.151	0.122	0.112	0.103	0.145
1.165	0.251	0.253	0.218	0.200	0.184	0.239
1.210	0.345	0.346	0.314	0.287	0.266	0.334
1.250	0.434	0.434	0.410	0.375	0.348	0.429
1.290	0.525	0.524	0.511	0.470	0.436	0.527
1.330	0.613	0.611	0.612	0.566	0.528	0.623
1.375	0.705	0.702	0.719	0.670	0.630	0.722
1.430	0.802	0.798	0.829	0.783	0.745	0.819
1.520	0.914	0.909	0.943	0.914	0.887	0.921
1.650	0.984	0.982	0.995	0.988	0.980	0.979

Table 9
Results of the kinetic analysis corresponding to the TG curve for P3/10.00/2.00

Kinetic function	Interpolation			Integration			CR			SY			MKN		
	γ	Log β	r^2	γ	Log β	r^2	γ	Log β	r^2	γ	Log β	r^2	γ	Log β	r^2
P3	10.00	2.00	1.0000	10.00	2.00	1.0000	11.91	2.48	0.9998	10.01	2.00	1.0000	9.36	1.79	1.0000
P4	6.48	1.52	1.0000	6.47	1.53	1.0000	–[a]	–	–	6.51	1.54	1.0000	5.63	1.21	0.9999
P2	17.23	2.97	1.0000	17.22	2.97	1.0000	17.99	3.16	1.0000	17.22	2.97	1.0000	16.82	2.86	1.0000
F0	39.34	5.95	1.0000	39.34	5.95	1.0000	39.50	5.99	1.0000	39.34	5.95	1.0000	39.19	5.91	1.0000
D1	83.96	11.96	1.0000	83.96	11.96	1.0000	84.00	11.97	1.0000	83.96	11.96	1.0000	83.93	11.96	1.0000
D6	77.75	10.44	0.9997	77.75	10.44	0.9997	77.80	10.45	0.9996	77.75	10.44	0.9996	77.71	10.43	0.9996
D2	90.21	13.00	0.9982	90.21	13.00	0.9982	90.24	13.00	0.9980	90.20	13.00	0.9980	90.17	12.99	0.9980
D4	92.75	12.94	0.9966	92.76	12.94	0.9966	92.78	12.95	0.9962	92.75	12.94	0.9962	92.72	12.93	0.9962
F1/2	44.40	6.81	0.9956	44.40	6.81	0.9956	44.52	6.84	0.9945	44.39	6.81	0.9945	44.27	6.78	0.9945
F2/3	46.30	7.13	0.9922	46.31	7.13	0.9922	46.41	7.16	0.9902	46.29	7.13	0.9902	46.18	7.10	0.9902
D3	97.95	13.80	0.9920	97.95	13.80	0.9920	97.97	13.80	0.9910	97.94	13.79	0.9910	97.92	13.79	0.9910
A4	9.12	2.05	0.9831	9.12	2.05	0.9831	11.28	2.60	0.9688	9.12	2.05	0.9611	8.42	1.82	0.9561
A3	13.60	2.67	0.9828	13.59	2.67	0.9828	14.75	2.96	0.9707	13.58	2.67	0.9680	13.08	2.52	0.9662
A2	22.71	3.95	0.9823	22.71	3.95	0.9823	23.16	4.06	0.9740	22.70	3.95	0.9734	22.39	3.87	0.9729
F1	50.45	7.83	0.9818	50.45	7.83	0.9818	50.54	7.85	0.9778	50.44	7.83	0.9777	50.34	7.80	0.9777
D5	115.51	16.67	0.9665	115.51	16.67	0.9665	115.51	16.68	0.9633	115.49	16.67	0.9633	115.47	16.67	0.9633
F3/2	57.54	9.01	0.9578	57.54	9.01	0.9578	57.59	9.03	0.9498	57.51	9.01	0.9497	57.44	8.99	0.9497
F2	65.61	10.35	0.9261	65.61	10.35	0.9261	65.64	10.36	0.9142	65.58	10.35	0.9141	65.52	10.34	0.9141

[a] Not considered (negative values of $Q(u)$).

kinetic models are often considered. Some of the pseudo-components defined in that way can decompose by reactions with low activation energies [42].

The results of the kinetic analysis of the simulated curve corresponding to P3/10.00/2.00 are shown in Table 9. In this case, six decimal figures for the values of α were considered. The interpolation and integration methods lead to kinetic parameters exactly equal to the expected ones, while there is a very slightly difference relatively to γ determined according to the SY method (10.01 instead of 10.00), which leads to a calculated curve with negative deviations from the original one (maximum difference of 0.01 in α). On the other hand, the methods of CR and of MKN originate kinetic parameters far from the starting ones. In addition, there is no compensation effect, since the corresponding calculated α versus θ curves do not fit the original points. To clarify this statement, it can be said that for $\gamma = 11.91$ and log $\beta = 2.48$ (CR) the reaction becomes complete at a normalized temperature near 3, and for $\gamma = 9.36$ and log $\beta = 1.79$ (MKN) a degree of transformation of about 0.45 is obtained at $\theta = 3.2$ (compare with curve d in Fig. 1).

All the considered methods foresee the possibility of the simulated curve to be approached by the kinetic

functions P2, P4, F0 or D1, besides P3. The relationship between the F1 model and the mechanisms of Avrami–Yerofeyev was discussed previously. In this case, the $g(\alpha)$ values corresponding to the mentioned functions are also related through the expressions

$$\ln g(\alpha)_{Pn} = \ln n + \frac{1}{n} \ln g(\alpha)_{F0} \tag{20}$$

$$\ln g(\alpha)_{D1} = \ln \tfrac{1}{2} + 2 \ln g(\alpha)_{F0} \tag{21}$$

Since the reaction occurs in a narrow range of temperatures (the points considered in the calculations correspond to normalized temperatures between 2.6 and 3.2), it is not possible to perform the discrimination among those mechanisms, as reported before for F1, A2, A3 and A4 [41]. In what concerns the results obtained, it may be concluded again that their accuracy strongly depends on the method used and on the values of the parameter γ. Thus, taking the kinetic parameters calculated by the integration method as reference, it can be stated that the interpolation and SY methods lead to equal or very similar values, with the possible exception of those associated to the P4 function when estimated with the latter method, according to the low γ involved. For the other two methods, only

Table 10
Results of the kinetic analysis corresponding to the TG curve for D4/10.00/2.00

Kinetic function[a]	Interpolation			Integration			CR			SY			MKN		
	γ	Log β	r^2	γ	Log β	r^2	γ	Log β	r^2	γ	Log β	r^2	γ	Log β	r^2
D4	9.94	1.98	1.0000	10.00	2.00	1.0000	10.78	2.28	0.9995	10.43	2.11	0.9992	10.23	2.01	0.9989
D2	9.34	2.23	0.9996	9.42	2.26	0.9995	10.28	2.57	0.9981	9.89	2.39	0.9969	9.68	2.28	0.9963
D3	11.11	2.42	0.9979	11.19	2.44	0.9981	11.83	2.67	0.9977	11.54	2.54	0.9981	11.36	2.45	0.9983
F0	1.06	0.20	0.9975	1.30	0.29	0.9981	–[b]	–	–	3.22	0.83	0.9646	4.16	1.22	0.9821
D1	7.97	1.71	0.9961	8.09	1.75	0.9955	9.17	2.14	0.9900	8.67	1.91	0.9850	8.43	1.78	0.9830
F1/2	2.40	0.72	0.9943	2.66	0.82	0.9956	–	–	–	4.19	1.24	0.9983	3.77	0.97	0.9964
D6	6.80	0.75	0.9937	6.93	0.80	0.9928	8.26	1.28	0.9841	7.63	0.99	0.9742	7.37	1.02	0.9704
F2/3	2.93	0.93	0.9908	3.18	1.02	0.9923	–	–	–	4.58	1.41	0.9981	4.18	1.15	0.9982
F1	4.13	1.39	0.9789	4.30	1.45	0.9807	6.56	2.28	0.9730	5.46	1.77	0.9821	5.11	1.55	0.9822
D5	15.29	3.95	0.9698	15.34	3.96	0.9704	15.67	4.08	0.9606	15.50	4.01	0.9608	15.37	3.95	0.9609
F3/2	6.10	2.12	0.9486	6.24	2.17	0.9509	7.79	2.73	0.9307	7.07	2.40	0.9319	6.78	2.24	0.9296
F2	8.28	2.93	0.9100	8.41	2.97	0.9123	9.45	3.34	0.8767	8.97	3.12	0.8737	8.74	3.00	0.8705

[a] The kinetic functions A2, A3, A4, P2, P3 and P4 are not considered, since both the interpolation and the integration methods originate negative γ values.

[b] Not considered (negative values of $Q(u)$).

the parameters corresponding to the D1 mechanism are very similar to those determined with the integration method, an observation that is directly related to the higher value of the parameter γ.

The results for the case D4/10.00/2.00 are presented in Table 10. All the methods allow for the correct mechanism to be determined, but the poor quality of the linear regressions obtained with the published procedures can be noted. Contrary to the previous case, which corresponds to the same kinetic parameters, the interpolation method does not lead to the correct γ and log β, but to slightly smaller values ($\gamma = 9.94$ and log $\beta = 1.98$). The normalized temperature ranges involved (1.15–2.2 for the present TG curve and 2.6–3.2 for the curve corresponding to P3/10.00/2.00) may explain these differences. As a matter of fact, according to Section 2.2 of this paper, when the parameter γ has a low value, the errors associated to the interpolations relatively to $1/\theta$ are larger for low values of θ (see also Table 2). In any case, there is an effective compensation between the two kinetic parameters and consequently the calculated curve approaches the original points very well (see Table 11). All the analyzed methods taken from the literature lead to parameter values higher than the starting ones and to differences larger than those determined by the interpolation method. As shown in Table 11, the curve corresponding to the solution

obtained by the CR method fits the simulated curve only in the beginning, and has important positive deviations for $\alpha > 0.3$. On the contrary, the calculated curve associated to the results obtained by the method of MKN is below the original. Finally, the values of γ and log β determined by the SY method, although far from the expected results, show some compensation effect, which leads to a good agreement between the calculated and the initial curves for intermediate and high α values.

From the results presented in this section, it may be concluded that the interpolation method, developed in this work, in spite of its simplicity, fulfills the objective of allowing the determination of the kinetic law and the kinetic parameters of reactions studied by linear temperature programming TG. In comparison with other methods already known from the literature, the interpolation method leads to as good or better results, both for mechanism discrimination and parameter accuracy. In particular, this new method is much superior for processes where γ and/or θ are low.

3.2. Experimental thermogravimetric curves

Some experimental thermogravimetric curves taken from the literature were also analyzed, namely, those corresponding to the decomposition of polytetrafluoroethylene (Teflon) in vacuum [43], the dehydroxylation

Table 11
Comparison between the simulated TG curve for D4/10.00/2.00 and the curves calculated from the results obtained by application of the mentioned methods

θ	α				
	Simulated, D4/10.00/2.00	Interpolation, D4/9.94/1.98	CR, D4/10.78/2.28	SY, D4/10.43/2.11	MKN, D4/10.23/2.01
1.15	0.091	0.092	0.088	0.085	0.083
1.25	0.147	0.148	0.146	0.139	0.135
1.35	0.214	0.215	0.216	0.205	0.198
1.45	0.292	0.292	0.299	0.282	0.272
1.55	0.380	0.379	0.394	0.370	0.356
1.65	0.474	0.473	0.498	0.466	0.448
1.75	0.574	0.572	0.607	0.568	0.545
1.85	0.674	0.671	0.716	0.671	0.644
1.95	0.771	0.768	0.820	0.771	0.741
2.05	0.859	0.856	0.910	0.862	0.832
2.20	0.963	0.960	0.996	0.968	0.944

of magnesium hydroxide [44], the decomposition of NH_4HF_2 [45] and the dehydration of calcium oxalate monohydrate [46]. The data points selected and the curves determined according to the best solutions obtained with the interpolation method are shown in Fig. 3. For the calculation of the normalized temperatures, it was considered that those experiments started

at room temperature except for the dehydration of $CaC_2O_4 \cdot H_2O$, in which case the temperature programme began at 40 °C (313 K) [46].

The results of the interpolation and integration methods, for the kinetic functions that correspond to the best fits in each case, are presented in Table 12. Both methods lead to equal or similar kinetic
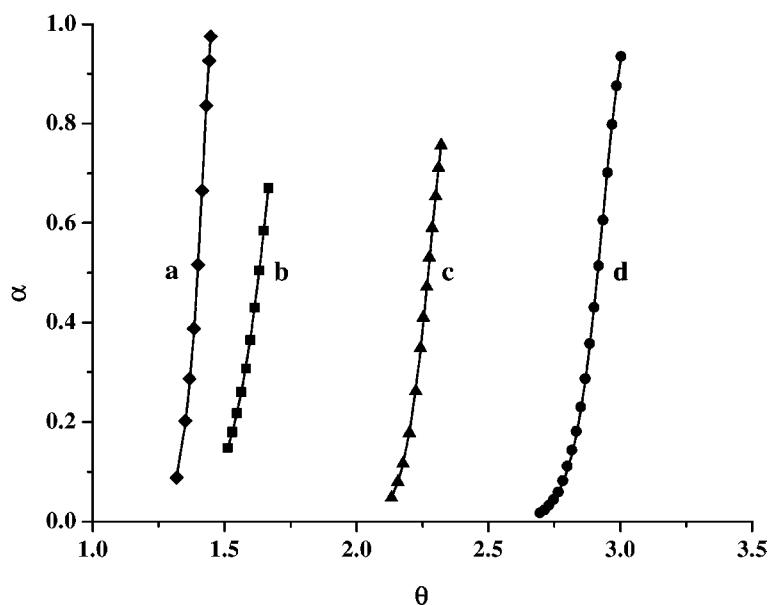

Fig. 3. Experimental thermogravimetric curves analyzed (a: dehydration of $CaC_2O_4 \cdot H_2O$; b: decomposition of NH_4HF_2; c: dehydroxylation of $Mg(OH)_2$; d: decomposition of Teflon (polytetrafluoroethylene)). The experimental points considered are shown as well as the lines corresponding to the best results obtained.

Table 12
Results of the kinetic analysis corresponding to the experimental TG curves (only the functions associated to the best fits are shown)

Reaction[a]	Kinetic function	Interpolation			Integration		
		γ	Log β	r^2	γ	Log β	r^2
a	F1/2	40.06	13.56	0.9989	40.06	13.56	0.9989
	F2/3	43.11	14.58	0.9986	43.11	14.58	0.9986
	D3	88.87	28.13	0.9986	88.87	28.13	0.9986
	D4	80.48	25.37	0.9983	80.48	25.37	0.9983
b	D4	52.08	13.93	0.9999	52.08	13.93	0.9999
	D2	50.57	13.96	0.9999	50.57	13.96	0.9999
	F1/2	24.97	7.44	0.9999	24.97	7.44	0.9999
	F2/3	26.09	7.78	0.9996	26.08	7.78	0.9996
	D3	55.11	14.83	0.9996	55.11	14.83	0.9996
c	F3/2	93.79	19.13	0.9998	93.78	19.13	0.9998
	D5	185.53	36.04	0.9994	185.52	36.03	0.9994
	F2	103.89	21.20	0.9988	103.88	21.20	0.9988
d	F1	126.31	19.86	0.9994	126.31	19.86	0.9994
	A2	60.48	10.13	0.9994	60.48	10.13	0.9994
	A3	38.60	6.89	0.9994	38.60	6.89	0.9994
	A4	27.71	5.28	0.9994	27.71	5.28	0.9994

[a] Dehydration of $CaC_2O_4 \cdot H_2O$, a; decomposition of NH_4HF_2, b; dehydroxylation of $Mg(OH)_2$, c; decomposition of Teflon (polytetrafluoroethylene), d.

parameters, since the γ values involved are not too small. Similar results (not presented) were also obtained with the classic techniques mentioned in this work.

The dehydration of calcium oxalate monohydrate data seem to correspond to a one-half order kinetics with $\gamma = 40.06$ and log $\beta = 13.56$, but the fit has not a very good quality. Thus, mechanisms F2/3, D3 and D4 must also be considered. The authors of the original paper [46] analyzed the data for a great number of kinetic laws, either by a differential method or by the CR method, and concluded that the mechanism F1/2 led to the best solution, as in the actual study. From the reported parameters, determined by the CR method, and keeping in mind the experimental conditions $T_0 = 313$ K and $\beta = 10$ K/min, we can calculate $\gamma = 40.14$ and log $\beta = 13.55$, which are values practically equal to those determined by us.

Dhar [45] analyzed NH_4HF_2 decomposition data by five methods, although most of them had a questionable degree of accuracy. Moreover, this author only considered kinetic expressions of the type $f(\alpha) = (1 - \alpha)^n$, that is to say F$n$ models. Using the CR method, he arrived to $n = 0.5$ and $E = 68.4$ kJ/mol, which corresponds to $\gamma = 28.1$, a value slightly

higher than the one obtained in this paper for the F1/2 function ($\gamma = 24.97$). However, as may be observed in Table 12, mechanisms D4 and D2 approach the experimental points equally well or even better. The difficult discrimination between the mentioned mechanisms is a direct consequence of the limited range of α in the experimental thermogravimetric curve (only values between 0.148 and 0.670 were considered).

Fong and Chen [44] studied the dehydroxylation of magnesium hydroxide and performed the kinetic analysis using data corresponding to α lower than approximately 0.8. The experimental points of run 1 of that work were considered for analysis, and we concluded by the interpolation method that a three-halves order kinetics with $\gamma = 93.79$ and log $\beta = 19.13$ gives the best fit to the experimental curve (see Table 12). This is in agreement with those authors, which presented reaction orders between 1.5 and 1.7, variable according to the used method, and E and A values equivalent to γ between 91.0 and 98.2 and log β between 18.6 and 21.1.

The decomposition of Teflon (polytetrafluoroethylene) was examined by Wen [43]. Considering a first-order reaction, he obtained $E = 301$ kJ/mol and $A = 9.45 \times 10^{15}$ s^{-1}, corresponding to $\gamma = 124$ and

log $\beta = 19.5$, respectively. The results determined by the methods developed in this paper are similar (see Table 12). However, the functions A2, A3 and A4 are also possible solutions, obviously with different kinetic parameters, according to the discussion already presented in Section 3.1.

4. Conclusions

A new method for kinetic analysis of dynamical thermogravimetric curves obtained under linear temperature programming, called the "interpolation method", was developed and validated in this paper. The method is based on the linear relationship between log $g(\alpha)$ and log $I(\gamma, \theta)$ for the kinetic function(s) corresponding to the correct mechanism(s) and on calculations of the values of the integral $I(\gamma, \theta)$ by linear interpolations, relatively to $1/\theta$ or γ, in a pre-built table. It proved to be a simple, fast and useful tool for that purpose, in comparison with other methods, particularly for low activation energy processes.

The errors associated to the linear interpolations mentioned above are generally small when the values of log I in the original table are calculated with increments of $\Delta\theta = 0.1$ and $\Delta\gamma = 5$, as considered in this work. They are relatively important only for low values of γ and θ.

A similar method, called the "integration method", which is based on the numerical calculation of the values of the normalized temperature integral $I(\gamma, \theta)$, was taken as reference. Comparison between the results obtained by the two methods (correct kinetic law and associated parameters γ and β) for a large number of simulated thermogravimetric curves led to the conclusion that they were identical. According to the linear interpolation errors mentioned in the previous paragraph, very small and still acceptable differences in the determined kinetic parameters were observed when the curves simultaneously correspond to low values of the parameter γ and of the variable θ.

It was verified that the CR and the MKN methods always lead to parameters more or less distant from the reference values. However, these differences are not significant for high γ values and seem to be non-admissible only for γ lower than about 20. On the contrary, the results obtained by the SY method are in general equal or close to the reference solutions, but it

can be stated that for γ values less than about 10 their quality is poor, of the same level as those determined by the other two literature methods considered.

In one of the cases presented (F1/6.87/2.99), according to the very low γ value involved and the previous comments, only the methods developed in this paper were able to discriminate the correct mechanism.

Application of the interpolation method to real experimental data collected from the literature, covering a wide range of parameters and kinetic models, showed good agreement between the results obtained and those reported in the original papers, determined by a number of techniques, and reinforced the main conclusions of the study performed with simulated curves.

In conclusion, the method presented in this work is very efficient to perform the kinetic analysis of processes studied by TG under linear temperature programming, particularly when they correspond to low activation energies and high reactivities, situations for which the known methods usually lead to important errors or even completely wrong solutions.

Acknowledgements

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