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IMPROVED ITERATIVE VERSION OF THE COATS-REDFERN METHOD TO EVALUATE NON-ISOTHERMAL KINETIC PARAMETERS

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Abstract

An improved version of the Coats-Redfern method of evaluating non-isothermal kinetic parameters is presented. The Coats-Redfern approximation of the temperature integral is replaced by a third-degree rational approximation, which is much more accurate. The kinetic parameters are evaluated iteratively by linear regression and, besides the correlation coefficient, the *F* test is suggested as a supplementary statistical criterion for selecting the most probable mechanism function. For applications, both non-isothermal data obtained by theoretical simulation and experimental data taken from the literature for the non-isothermal dehydration of $Mg(OH)_2$ have been processed.

Keywords: evaluation of kinetic parameters, *F* test, improved Coats-Redfern method, linear regression, non-isothermal kinetics

Introduction

In the past few decades, determination of the mechanism function and calculation of the kinetic parameters from non-isothermal TG, DTA and DSC data have been subjects of considerable interest. Consequently, a considerable number of methods have been suggested whereby kinetic parameters can be evaluated from the data of non-isothermal experiments.

In 1964, Coats and Redfern presented an integral method [1] which has since become one of the most widely used methods in non-isothermal kinetic analysis. Despite the longevity of the Coats-Redfern method, not much has been done to improve its performance. We refer to the following aspects: i) the Coats-Redfern approximation of the temperature integral is not very accurate [2–6]; ii) the selection of the most probable mechanism function, based on the correlation coefficient of the linear

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regression analysis, does not seem to be always statistically well-founded, since the maximum correlation coefficient may differ insignificantly from its lower values [7, 8]; and iii) the graphical procedure suggested by the Coats-Redfern method leads to single-valued kinetic parameters (E and ln$A$), whereas in a proper linear regression analysis it is also necessary to give the corresponding confidence intervals for the evaluated parameters [7–10].

In this work, we discuss the above-mentioned problems and develop an improved iterative version of the Coats-Redfern method as a final outcome.

Theory

In non-isothermal kinetics, for the most usual case of a linear heating program corresponding to a constant heating rate (β), the dependence of the reaction rate on temperature (T) and degree of conversion (α) is described by the well-known differential equation [2, 3]

$$\mathrm{d}\alpha/\mathrm{d}T = (A/\beta)f(\alpha)\exp[-E/RT] \tag{1}$$

where A is the pre-exponential factor, E is the activation energy, and $f(\alpha)$ is the differential conversion function, which characterizes the reaction mechanism.

Through variable separation and integration, Eq. (1) leads to

$$g(\alpha) \equiv \int_0^\alpha \mathrm{d}\alpha/f(\alpha) = (A/\beta)\int_0^T \exp[-E/RT]\mathrm{d}T \tag{2}$$

where $g(\alpha)$ is the integral conversion function.

The integral on the right-hand side of Eq. (2) has no exact analytical solution, but it can be approximated as follows [6, 11]:

$$\int_0^T \exp[-E/RT]\mathrm{d}T = (R/E)T^2\exp[-E/RT]Q(x) \tag{3}$$

where x=E/RT and $Q(x)$ is a function which changes slowly with x and is close to unity. An alternative way to express the temperature integral [2–5, 12] is

$$\int_0^T \exp[-E/RT]\mathrm{d}T = (E/R)p(x) \tag{4}$$

where

$$p(x) = \int_{x}^{\infty} (1/x^2)\ \exp[-x]\mathrm{d}x \qquad (5)$$

If Eqs (3) and (4) are taken into account, the following relationship between $p(x)$ and $Q(x)$ is obtained:

$$p(x) = x^{-2}\exp[-x]Q(x) \qquad (6)$$

From relationship (3) and Eq. (2), one obtains

$$g(\alpha) = (AR/E\beta)T^2\exp[-E/RT]Q(x) \qquad (7)$$

which is the starting equation for many integral methods of evaluating non-isothermal kinetic parameters.

The Coats-Redfern method is based upon the following approximation [1]:

$$Q_{\mathrm{C-R}}(x) = (x-2)/x = 1 - 2RT/E \qquad (8)$$

which has rather a low accuracy [2–6]; for example, the relative error of this approximation is –1.38% x=20, while for x=10 it becomes –5.18% [4, 6]. On inserting approximation (8) into Eq. (7) and taking logarithms, one obtains

$$\ln[g(\alpha)/T^2] = \ln[(AR/E\beta)\ (1 - 2RT/E)] - E/RT \qquad (9)$$

Since in general $2RT/E \ll 1$ and it exhibits a small variation with T, for practical considerations it is assumed that the term $(1-2RT/E)$ is approximately constant and equal to unity. Thus, for a given form of $g(\alpha)$, the plot of $\ln[g(\alpha)/T^2$ *vs.* $1/T$ gives a straight line whose slope and intercept allow an estimation of the values of the activation energy and pre-exponential factor, respectively. In order to identify the most probable mechanism function, $g(\alpha)$, Coats-Redfern proposed the choice of that one which ensures the best linearity, corresponding to the maximum value of the correlation coefficient [1].

The first step in improving the method of Coats and Redfern is to choose a more accurate approximation for the temperature integral. In the literature, one can find several approximations which are more accurate that the Coats-Redfern approximation [2–6]. For our purposes, we consider the following third-degree rational approximation to be appropriate [4, 6]:

$$Q(x) = (x^3 + 10x^2 + 18x)\ /\ (x^3 + 12x^2 + 36x + 24) \qquad (10)$$

which ensures an error lower than $1.6\cdot10^{-3}$% for $x \geq 10$.

After taking of logarithms and rearrangement, Eq. (7) becomes

$$\ln[g(\alpha)/T^2] - \ln[Q(E/RT)] - \ln(AR/E\beta) + E/RT = 0 \qquad (11)$$

For a given form of $g(\alpha)$, the kinetic parameters can be evaluated on the basis of Eq. (11) by applying the least squares method [9, 10, 13]. In this case, the sum of the squares of the residual terms, S_{res}, should be written as

$$S_{res} = \sum_{i=1}^{N} \{\ln[g(\alpha_i)/T_i^2] - \ln[Q(E/RT_i)] - \ln(AR/E\beta) + E/RT_i\}^2 \tag{12}$$

where N is the number of experimentally determined data points, (α_i, T_i). The values of the kinetic parameters A and E may be found from the condition of the minimum in S_{res}, which yields the system of non-linear equations

$$\partial S_{res}/\partial A = \partial S_{res}/\partial E = 0 \tag{13}$$

Finding a numerical solution to this system is a quite difficult problem, which requires complicated computational procedures [10]. These difficulties can be bypassed, however, by considering an iterative procedure which transforms the evaluation of the kinetic parameters from a non-linear regression [14].

To develop the iterative procedure, let us introduce the notations

$$\ln(AR/E\beta) = a \tag{14}$$

and

$$E/R = b \tag{15}$$

With these notations, S_{res} becomes

$$S_{res} = \sum_{i=1}^{N} \{\ln[g(\alpha_i)/T_i^2] - \ln[Q(b/T_i)] - a + b/T_i\}^2 \tag{16}$$

The minimization of S_{res} with respect to a and b can be solved by the following iterative procedure.

Iteration (1)

To a first approximation, we consider $Q(b/T) \cong 1$, and thus from Eq. (16) one obtains

$$S_{res_1} = \sum_{i=1}^{N} \{\ln[g(\alpha_i)/T_i^2] - a + b/T_i\}^2 \tag{17}$$

The condition of the minimum in S_{res_1} leads to the system of linear equations

$$\partial S_{res_1}/\partial a = \partial S_{res_1}/\partial b = 0 \tag{18}$$

which can easily be solved to obtain a first estimate for a_1 and b_1. In this way, the kinetic parameters (A_1 and E_1) can be determined from Eqs (14) and (15).

It should be emphasized that the graphical procedure suggested by Coats and Redfern in fact gives the same kinetic parameters as obtained from system (18).

Iteration (2)

For this step, we assume that the following approximation is valid:

$$\ln[Q(b/T_i)] \cong \ln[Q(b_1/T_i)] \tag{19}$$

and therefore Eq. (16) becomes

$$S_{\mathrm{res}_2} = \sum_{i=1}^{N} \left\{\ln[g(\alpha_i)/T_i^2] - \ln[Q(b_1/T_i)] - a + b/T_i\right\}^2 \tag{20}$$

The new estimates of the parameters a and b can be obtained by minimizing S_{res_2} with respect to a and b. This gives the system of linear equations

$$\partial S_{\mathrm{res}_2}/\partial a = \partial S_{\mathrm{res}_2}/\partial b = 0 \tag{21}$$

whose solutions are a_2 and b_2.

Iteration (k)

The approximation $\ln[Q(b/T_i)]$ is

$$\ln[Q(b/T_i)] \cong \ln[Q(b_{k-1}/T_i)] \tag{22}$$

where b_{k-1} is the estimation of b obtained in iteration (k–1). If this approximation is inserted into Eq. (16), one obtains

$$S_{\mathrm{resk}} = \sum_{i=1}^{N} \left\{\ln[g(\alpha_i)/T_i^2] - \ln[Q(b_{k-1}/T_i)] - a + b/T_i\right\}^2 \tag{23}$$

The final estimation of the parameters a and b can be obtained by solving the system of linear equations

$$\partial S_{\mathrm{resk}}/\partial a = \partial S_{\mathrm{resk}}/\partial b = 0 \tag{24}$$

The values of a_k and b_k obtained in this way allow determination of the final values of the kinetic parameters (A_k and E_k) on the basis of Eqs (14) and (15).

The minimization of S_{resk} is similar to the graphical procedure elaborated by Coats-Redfern. Thus, for a given form of $g(\alpha)$, the plot of $\{\ln[g(\alpha)/T^2]–\ln[Q(b_{k-1}/T_i)]\}$ *vs.* $1/T$ gives a straight line whose slope and intercept allow estimation of the values of

a_k and b_k, and consequently the values of the pre-exponential factor (A_k) and activation energy (E_k), respectively.

The iterative procedure is stopped when the following two conditions are fulfilled:

$$|a_k - a_{k-1}|/a_k < e_a \tag{25}$$

and

$$|b_k - b_{k-1}|/b_k < e_b \tag{26}$$

For application, we have used $e_a=e_b=0.001$, which means that the difference between the last two estimations is lower than 10^{-5}%.

As the selection of the most probable mechanism function on the basis of only the correlation coefficient (r) of the linear regression analysis does not always seem to be statistically well-founded, i.e. the maximum correlation coefficient may differ insignificantly from its lower values [7, 8], in this new version of the Coats-Redfern method, besides the correlation coefficient, the F-ratio determined by applying the F test [9, 10, 13] has been used as a supplementary statistical criterion to identify the most probably mechanism function, $g(\alpha)$. Moreover, it will be shown that the residual mean square S_{yx^2} [9, 13] cannot be used as a statistical criterion for selecting the most probable mechanism function. Details are presented in the Appendix.

Applications and discussion

For applications, both non-isothermal data obtained by theoretical simulation and experimental data taken from the literature for the non-isothermal dehydration of $Mg(OH)_2$ have been used. The most common mechanism functions, $g(\alpha)$, used for applications are listed in Table 1.

Table 1 Usual mechanisms from the literature and the corresponding forms of $g(\alpha)$

No.	Mechanism	$g(\alpha)$	Observations
1.	Pm Power law	$\alpha^{1/m}$	$m = 1; 2; 3$ and 4
2.	An Avrami-Erofeev	$[-\ln(1-\alpha)]^{1/n}$	$n = 3/2; 2; 3$ and 4
3.	R2 Contracting surface	$2[1-(1-\alpha)^{1/2}]$	
4.	R3 Contracting volume	$3[1-(1-\alpha)^{1/3}]$	
5.	Fn n^{th}-order reaction	$[1-(1-\alpha)^{1-n}]/(1-n)$	$g(\alpha)=-\ln(1-\alpha)$ if $n = 1$
6.	D1 1-D diffusion	α^2	
7.	D2 2-D diffusion	$\alpha+(1-\alpha)\ln(1-\alpha)$	
8.	D3 3-D diffusion (Jander Eq.)	$[1-(1-\alpha)^{1/3}]^2$	
9.	D4 3-D diffusion (Ginstling-Brounshtein Eq.)	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	

Theoretical data

Three well-known mechanism functions have been employed to obtain simulated non-isothermal data. These three cases are: 1. the equation for contracting volume (R3); 2. the Avrami-Erofeev equation for n=3 (A3); and 3. the Jander equation for 3-D diffusion (D3). In every case, N=39 data points (α,T) with the degree of conversion ranging from 0.025 to 0.975 have been generated by using in Eq. (7) the following values for the kinetic parameters: E=160 kJ mol^{-1} and A=6·10^{13} min^{-1}. A usual value of 10 K min^{-1} for the heating rate (β) was considered.

The values of the kinetic parameters evaluated by the improved Coats-Redfern method and corresponding to cases 1, 2 are 3 are given in Table 2. To fulfil conditions (25) and (26), three iterations were necessary; the indices of E and A refer to the number of the iteration. In order to perform the numerical calculations required by the minimization of S_{res}, the 'Linear Regression' package of the Mathematica software system was used [15, 16].

Table 2 reveals that, after three iterations, the obtained values of the kinetic parameters are identical with those used in the simulation. It should also be mentioned that, between the values of the kinetic parameters calculated in the first iteration and the last iteration, there are some differences, which are more significant for the pre-exponential factor, i.e. for every case the value of A_1 is about 10% less than the final value (A_3).

The effect of the differences between the Coats-Redfern kinetic parameters (A_1 and E_1) and the kinetic parameters obtained by the improved Coats-Redfern method (A_3 and E_3) can be illustrated graphically. Figure 1 shows for cases 1–3 the simulated (α,T) data points and the α *vs.* T curves generated with A_1 and E_1, whereas Fig. 2 presents the corresponding data points and the α *vs.* T curves generated with A_3 and E_3. It is obvious from these illustrations that the α *vs.* T curves generated with A_3 and E_3 fit the 39 data points much better than do the α *vs.* T curves generated by using A_1 and E_1.

At the same time, the correctness of the fit can also be appreciated quantitatively by using the arithmetic mean of the absolute values of the relative errors (S_{abs}), i.e.

$$S_{abs} = (1/N)\sum_{i=1}^{N}|(\alpha_{calc,i} - \alpha_{sim,i})/\alpha_{sim,i}| \tag{27}$$

In the above expression, α_{sim} is the value of α obtained by numerical simulation, α_{calc} is the value of α determined by using the evaluated kinetic parameters in Eq. (7), and the significance of N has been clarified previously. It is worth mentioning that, the smaller the value of S_{abs}, the better the goodness of the fit. Table 3 shows the values of S_{abs} for cases 1, 2 and 3, as determined with the kinetic parameters obtained by the Coats-Redfern method and by the improved Coats-Redfern method. Obviously, a better correlation between α_{calc} and α_{sim} can be observed when the kinetic parameters obtained with the improved method are involved.

Table 2 Values of the kinetic parameters calculated with the improved Coats-Redfern method and corresponding to cases 1, 2 and 3; the indices of *E* and *A* refer to the number of iterations

Case no.	$g(\alpha)$	E_1/kJ mol^{-1}	A_1/min^{-1}	E_2/kJ mol^{-1}	A_2/min^{-1}	E_3/kJ mol^{-1}	A_3/min^{-1}
1.	$3[1-(1-\alpha)^{1/3}]$	159.742	$5.363\cdot 10^{13}$	160.000	6.001·1013	160.000	$6.000\cdot 10^{13}$
2.	$[-\ln(1-\alpha)]^{1/3}$	159.730	$5.350\cdot 10^{13}$	160.000	6.001·1013	160.000	$6.000\cdot 10^{13}$
3.	$[1-(1-\alpha)^{1/3}]^2$	159.782	$5.412\cdot 10^{13}$	160.000	6.001·1013	160.000	$6.000\cdot 10^{13}$

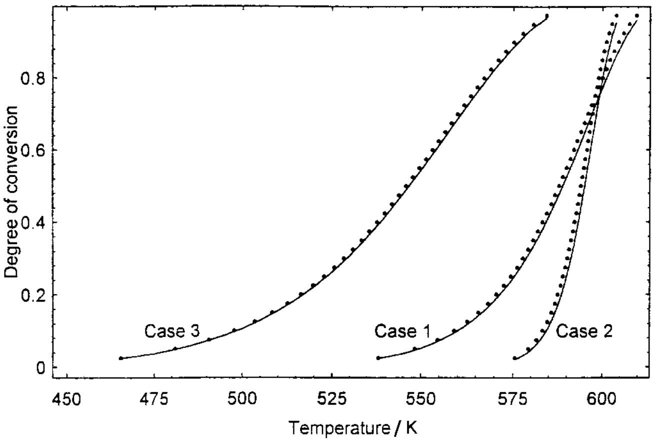

Fig. 1 Simulated (α,T) data points (...) and the α *vs.* T curves generated with the kinetic parameters evaluated by using the classical Coats-Redfern method for Cases 1–3

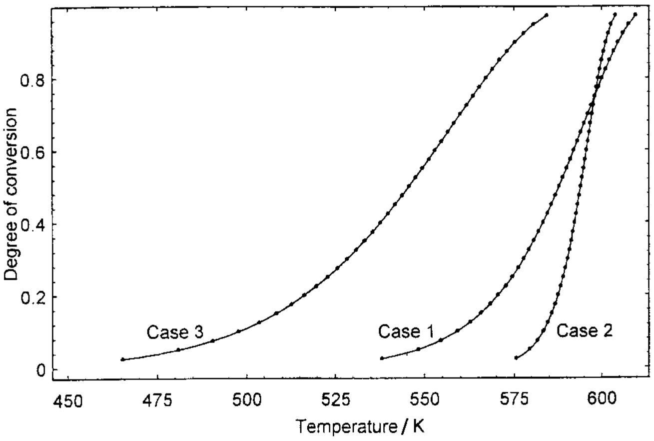

Fig. 2 Simulated (α,T) data points (...) and the α *vs.* T curves generated with the kinetic parameters evaluated by using the improved Coats-Redfern method for Cases 1–3

Table 3 The values of S_{abs} for cases 1, 2 and 3, determined with the kinetic parameters obtained by the Coats-Redfern method and the improved Coats-Redfern method

Case no.	S_{abs} Coats-Redfern method	S_{abs} improved Coats-Redfern method
1.	$4.110\cdot10^{-2}$	$7.449\cdot10^{-6}$
2.	$1.094\cdot10^{-1}$	$1.790\cdot10^{-5}$
3.	$1.911\cdot10^{-2}$	$5.544\cdot10^{-6}$

Non-isothermal dehydration of $Mg(OH)_2$

The thermogravimetric data for the dehydration of magnesium hydroxide have been taken from Ref. 17. Evaluation of the kinetic parameters is made for case 1, in which the value of N is 21, with the degree of conversion ranging from 0.0251 to 0.7950. The results obtained by linear regression after three iterations, for the most usual mechanisms from the literature, are given in Table 4.

The most probable value of n corresponding to the Fn model is determined from the condition of the maximum in the value of the F-ratio, i.e.

$$\mathrm{d}(F - \mathrm{ratio}(n))/\mathrm{d}n = 0 \tag{28}$$

In order to describe the functional relationship between n and the F-ratio, a 4th-degree polynominal was involved by using the ‘Polynominal’ package of Mathematica [16]. By solving Eq. (28) numerically, a value of 1.777 was found for n. The above procedure is illustrated graphically in Fig. 3, while the regression results obtained for n=1.777 are listed in Table 5.

From the data presented in Tables 4 and 5, it can be inferred that the most probable mechanism function is Fn with n=1.777. This result is supported by two of the statistical criteria used for selection, i.e. r and the F-ratio. At this point, it should be emphasized that the F-ratio seems to be a more suitable statistical criterion than the correlation coefficient, as its value depends more significantly on the form of the mechanism function.

In Refs 7 and 18, Vyazovkin *et al.* suggested that the residual mean squares can be employed to determine the most probable mechanism function. The use of S_{xy}^2 for our particular case (Table 4) yields the Avrami-Erofeev mechanism with n=4 (A4), a result which is not supported by the corresponding values for r and the F-ratio. We consider, therefore, that S_{xy}^2 cannot be used as a statistical criterion for determining the most probable mechanism function, $g(\alpha)$; additional details are given in the Appendix.

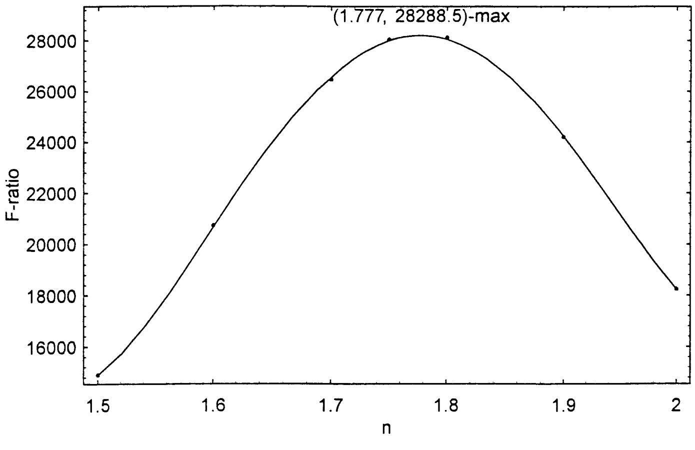

Fig. 3 Dependence of the F-ratio on n for $Mg(OH)_2$

Table 4 Linear regression results obtained for the usual mechanisms after three iterations for the thermal dehydration of $Mg(OH)_2$

No.	Mechanism	E/kJ mol^{-1}	ln$A$/min^{-1}	r	S^2_{xy}	F-ratio
1.	Pm; m=1	175.766±13.783	29.607±2.550	0.98693	0.028456	712.5
2.	Pm; m=2	82.898±6.922	12.524±1.281	0.98522	0.007177	628.4
3.	Pm; m=3	52.101±4.633	6.684±0.857	0.98328	0.003215	554.0
4.	Pm; m=4	36.811±3.488	3.700±0.645	0.98108	0.001822	488.0
5.	An; n=3/2	137.127±5.057	22.901±0.936	0.99706	0.003831	3220.8
6.	An; n=2	100.350±3.807	16.036±0.704	0.99689	0.002172	3043.0
7.	An; n=3	63.675±2.557	9.072±0.473	0.99652	0.000979	2717.2
8.	An; n=4	45.432±1.931	5.523±0.357	0.99611	0.000558	2426.3
9.	R2	192.247±10.966	32.847±2.029	0.99302	0.018015	1346.3
10.	R3	198.195±9.891	34.014±1.830	0.99464	0.014653	1759.2
11.	Fn; n=1	210.791±7.556	36.481±1.398	0.99723	0.008552	3409.6
12.	Fn; n=1.5	231.446±3.969	40.517±0.734	0.99936	0.002359	14900.2
13.	Fn; n=2	254.165±3.939	44.944±0.729	0.99948	0.002324	18242.0
14.	Fn; n=3	305.227±14.894	54.862±2.755	0.99488	0.033230	1839.9
15.	D1	361.900±27.500	63.154±5.088	0.98771	0.113288	758.7
16.	D2	382.680±24.130	66.496±4.464	0.99149	0.087221	1101.8
17.	D3	406.802±19.716	69.665±3.648	0.99495	0.058233	1864.9
18.	D4	390.675±22.670	66.541±4.194	0.99278	0.076984	1301.0

Table 5 Results obtained by linear regression for the thermal dehydration of $Mg(OH)_2$ and corresponding to the most probable mechanism function (Fn; n=1.777)

Iteration	n	E/kJ mol^{-1}	ln$A$/min^{-1}	r	S_{xy}^2	F-ratio
1.	1.777	243.563±3.034	42.838±0.561	0.99966	0.001379	28234.2
2.	1.777	243.783±3.034	42.922_5±0.561	0.99966	0.001379	28288.6
3.	1.777	243.783±3.034	42.922_4±0.561	0.99966	0.001379	28288.6

Table 6 shows the values of the kinetic parameters evaluated in the present work and, for comparison, two sets of values given in Refs 7 and 17 for the same experimental data. For each set of kinetic parameters, the quality of the fit is appreciated quantitatively by the sum

$$S_{abs} = (1/N) \sum_{i=1}^{N} | (\alpha_{calc,i} - \alpha_{exp,i})/\alpha_{exp,i} | \qquad (29)$$

where α_{exp} is the experimental value of the degree of conversion and α_{calc} is the value determined by using the evaluated kinetic parameters in Eq. (7).

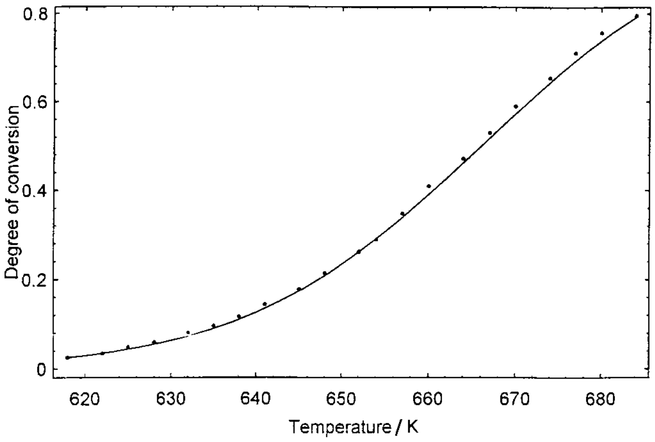

Fig. 4 Experimental (α,T) data points (...) for $Mg(OH)_2$ and the α *vs.* T curve generated with the kinetic parameters evaluated by using the classical Coats-Redfern method

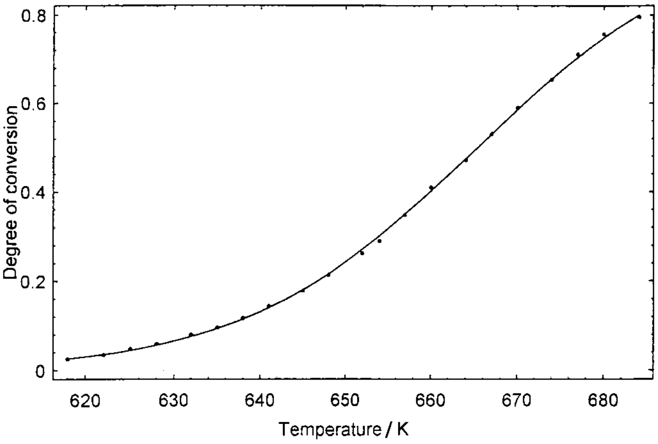

Fig. 5 Experimental (α,T) data points (...) for $Mg(OH)_2$ and the α *vs.* T curve generated with the kinetic parameters evaluated by using the improved Coats-Redfern method

Table 6 Kinetic parameters obtained by various methods for the thermal dehydration of $Mg(OH)_2$; the appropriate confidence intervals are not presented

Method	n	E/kJ mol^{-1}	A/min^{-1}	S_{abs}	Reference
Coats-Redfern	1.777	243.563	$4.021\cdot10^{18}$	$3.312\cdot10^{-2}$	present work
Improved Coats-Redfern	1.777	243.783	$4.375\cdot10^{18}$	2.308·10–2	present work
Fong and Chen	1.5867	221.857	$7.109\cdot10^{16}$	7.935·10–2	17
Vyazovkin and Lesnikovich	1.725	241.442	$2.761\cdot10^{18}$	2.301·10–2	7

It can be concluded from the data presented in Table 6 that the kinetic parameters evaluated by the improved Coats-Redfern method and by the method of Vyazovkin and Lesnikovich [7] give the best description to the experimental data: in both cases, the values of S_{abs} are low and very close. A satisfactory description is given by the kinetic parameters evaluated by the classical Coats-Redfern method, while the method suggested by Fong and Chen [17] furnishes kinetic parameters which describe the experimental data less accurately. It should also be mentioned that the agreement between the kinetic parameters evaluated by various methods is satisfactory.

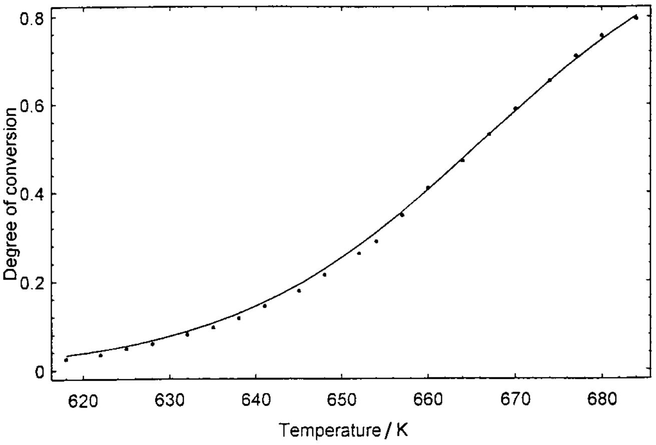

Fig. 6 Experimental (α,T) data points (...) for $Mg(OH)_2$ and the α *vs.* T curve generated with the kinetic parameters evaluated by using the method of Fong and Chen

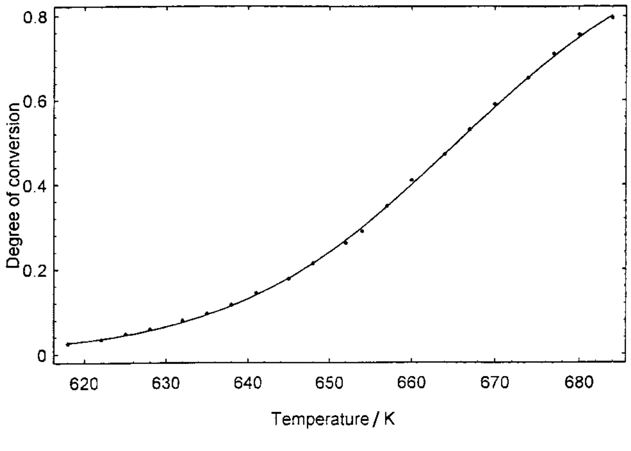

Fig. 7 Experimental (α,T) data points (...) for $Mg(OH)_2$ and the α *vs.* T curve generated with the kinetic parameters evaluated by using the method of Vyazovkin and Lesnikovich

In order to illustrate the afore-mentioned observations graphically, Figs 4–7 depict the experimental data points and the α *vs.* T curves generated by substituting the kinetic parameters from Table 6 in Eq. (7). It can be observed that, the lower the value of S_{abs}, the better the fit.

Conclusions

(1) An improved iterative version of the classical Coats-Redfern method has been presented.

(2) Besides the correlation coefficient, the F-ratio is suggested as a supplementary statistical criterion to determine the most probable mechanism function.

(3) The new method has been applied successfully in the processing of both non-isothermal data obtained by theoretical simulation and experimental data taken from the literature on the non-isothermal dehydration of $Mg(OH)_2$.

(4) The values of the kinetic parameters for the dehydration of $Mg(OH)_2$ are in good agreement with those given in the literature.

Appendix

In linear regression, we consider the problem of fitting a set of N data points (x_i,y_i)=1, 2, ...N to a straight-line model [9, 10, 13]:

$$y = a + bx \tag{A1}$$

For every pair of values (x_i,y_i), it is assumed that x_i (independent variable) is fixed, and that y_i (dependent variable) is a random variable. It is usually assumed further that the random errors are normally distributed with zero mean; thus, we obtain estimates of the parameters a and b by minimizing the sum of the squares of the residual terms [9, 10, 13]

$$S_{res} = \sum_{i=1}^{N} (y_i - a - bx)^2 \tag{A2}$$

with respect to a and b. This gives the system of linear equations

$$\partial S_{res}/\partial a = \partial S_{res}/\partial b = 0 \tag{A3}$$

which can be solved in order to evaluate the model parameters a and b.

For the particular case of the improved Coats-Redfern method, the dependent variable (y) becomes $\{\ln[g(\alpha)/T^2]-\ln[Q(b_{k-1}/T)]\}$, while the independent variable is $1/T$.

In order to identify the most probable mechanism function, $g(\alpha)$, besides the correlation coefficient, we suggest the F-ratio as a supplementary statistical criterion.

The *F*-ratio is evaluated by performing the *F* test [9, 10, 13, 16]. In this way, the value of the *F*-ratio is expressed as

$$F - \text{ratio} = S_{\text{reg}}/S_{xy^2} \tag{A4}$$

where

$$S_{\text{reg}} = b\sum_{i=1}^{N} (x_i - \bar{x})(y_i - \bar{y}) \tag{A5}$$

and

$$S_{xy^2} = [1/(N-2)]\, S_{\text{res}} \tag{A6}$$

is the residual mean square. In relationship (A5), $\bar{x}$ and $\bar{y}$ denote the means of x and y, respectively.

The *F* test provides a comparison of the given model with a smaller one including only a constant term. Actually, we test the null hypothesis (b=0) *vs*. the alternative hypothesis ($b\neq0$) [9, 16]. If the value of the *F*-ratio is large, the null hypothesis supporting the smaller model is rejected. It should also be mentioned that, the higher the value of the *F*-ratio, the better the fit, and thus the *F*-ratio can be used as a statistical criterion to determine the most probable mechanism model.

The numerical calculation required by the minimization of S_{res} is performed by using the 'Linear Regression' package of the Mathematica® software system [16].

Besides the values of a, b, r, S_{res}, S_{xy^2} and the *F*-ratio, this package provides the confidence intervals for a and b [16]. For all applications, a confidence level of 95% has been considered.

Finally, it should be stressed that the residual mean square, S_{xy^2}, which is, in fact, an unbiased estimator of the variance of the distribution, σ^2, [9] cannot be used as a statistical criterion for selecting the most probable mechanism function, $g(\alpha)$, as suggested by Vyazovkin *et al.* [7, 18]. This is due to the fact that, for different mechanism functions, we have different magnitudes of the values of the dependent variable $y=\ln[g(\alpha)/T^2]-\ln[Q(b_{k-1}/T_i)]$, and consequently of S_{xy^2} [19]. The results presented in Tables 4 and 5 support the above statement.

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