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DISCRIMINATION OF THE KINETIC MODEL OF OVERLAPPING SOLID-STATE REACTIONS FROM NON-ISOTHERMAL DATA

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A method has been developed that allows the deconvolution of up to 15 overlapping solid-state reactions without previous assumptions. Both the kinetic parameters and the reaction mechanisms fitted by the unit reactions can be determined from a series of non-isothermal experiments carried out at different heating rates.

During recent years, the kinetic analysis of complex reactions has received the attention of a great number of authors [1–4]. Elder [5], Agrawall [6] and other workers have shown that the kinetic analysis of DTG or DTA traces obtained from the sum of a set of individual reactions leads to important errors in the determination of the activation energies. Ozawa [7] and Flynn [8] have analysed the effect of the heating rate on overlapping reactions in order to separate the individual steps. They have concluded that mutually independent reactions with large differences in activation energy can be deconvoluted by increasing or decreasing the heating rate. However, they cannot be separated if their activation energies are of the same order of magnitude. In such a case, the problem can only be resolved mathematically. It must be pointed out that a number of computer programs for deconvolution have been proposed in the literature [9–10], but their application is restricted, to our knowledge, to "*n*-order reactions". Therefore, it would be interesting to develop a general method for deconvoluting overlapping reactions without restrictions with regard to the kinetic model satisfied by the unit reactions.

Previous papers have shown [11, 12] that non-isothermal curves of single solid-state reactions must satisfy the kinetic equations developed for the kinetic analysis of "*n*-order reactions", even if they follow a quite different mechanism. The values calculated for the apparent reaction order, *n*, and the ratio of the apparent *n*-order activation energy and the real one are included in Table 1. These data lead to the

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Table 1 Values of the ratio of the apparent activation energy and the real one (Ea/E) for the most common mechanisms in solid-state reactions approximated by n-order kinetic models

Mechanism		$f(\alpha)$	$g(\alpha)$	E_a/E	n_a
Phase boundary-controlled reaction (contracting area)	R2	$(1-\alpha)^{1/2}$	$2(1-(1-\alpha)^{1/2}$	1	1/2
Phase boundary-controlled reaction (contracting volume)	R3	$(1-\alpha)^{2/3}$	$3(1-(1-\alpha)^{1/3})$	1	2/3
Random nucleation. Unimolecular decay law	F1	$(1-\alpha)$	$-\ln(1-\alpha)$	1	1
Two-dimensional growth of nuclei (Avrami equation)	A2	$2(-\ln(1-\alpha)^{1/2})(1-\alpha)$	$(-\ln(1-\alpha))^{1/2}$	2	1
Three-dimensional growth of nuclei (Avrami equation)	A3	$3(-\ln(1-\alpha)^{2/3})(1-\alpha)$	$(-\ln(1-\alpha))^{1/3}$	3	1
One-dimensional diffusion	D1	$1/2\alpha$	α^2	0.475	0
Two-dimensional diffusion	D2	$1/(-\ln(1-\alpha))$	$(1-\alpha)\ln(1-\alpha)+\alpha$	0.475	0.3
Three-dimensional diffusion (Jander equation)	D3	$\dfrac{3(1-\alpha)^{2/3}}{2(1-(1-\alpha)^{1/3})}$	$(1-(1-\alpha)^{1/3})^2$	0.475	2/3
Three-dimensional diffusion (Ginstlein equation)	D4	$3/2((1-\alpha)^{-1/3}-1)$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	0.475	0.43

conclusion that, unfortunately, the actual mechanisms of solid-state reactions cannot be discriminated from the kinetic analysis of a single TG or DTG trace. The scope of the present paper is to take advantage of this misfortune in order to propose a general method for the deconvolution of mutually independent overlapping solid-state reactions and for the discrimination of the kinetic model satisfied by the unit reactions.

Theoretical

It is easy to show that the overall reacted fraction α of a series of simultaneous and mutually independent reactions depends on the reacted fractions of the unit reactions, α_i, according to the following expression:

$$\alpha = \Sigma\lambda_i\alpha_i \tag{1}$$

where λ_i is the ratio of the final weight loss of unit reaction i and the final weight loss of the overall process. It is evident that $\Sigma\lambda_i = 1$, provided that $\alpha = \alpha_i = 1$ when the overall reaction is complete.

On the other hand, if Eq. (1) is taken into account, the overall reaction rate can be expressed as a function of the rates of the individual reactions:

$$\frac{d\alpha}{dt} = \Sigma\lambda_i\frac{d\alpha_i}{dt} = \Sigma\lambda_i K_i f_i(\alpha_i) \tag{2}$$

where $f_i(\alpha_i)$ is a function depending on the actual reaction mechanism of reaction i, and K_i is its corresponding reaction rate constant, given by the Arrhenius law:

$$K_i = A_i \exp(-E_i/RT) \tag{3}$$

If the temperature of the sample is increased at a constant rate $\beta = dT/dt$, Eq. (2) can be integrated:

$$\Sigma\lambda_i g_i(\alpha_i) = \sum\frac{\lambda_i A_i}{\beta}\int_0^T \exp(-E_i/RT)\,dt \tag{4}$$

A being the preexponential Arrhenius factor; E is the activation energy: and $g(\alpha)$ is a function depending on the reaction mechanism and the subscript i refers to unit reaction i. The functions $f(\alpha)$ and $g(\alpha)$ used in the literature to describe solid-state reactions are listed in Table 1.

The integral of the right-hand side of Eq. (4) cannot be expressed in a closed form [13, 14], but must be calculated from numerical methods. The integration of the Arrhenius equation has been carried out in this paper with an accuracy better than $10^{-5}\%$ by means of the fourth-order rational approximation proposed by Senung and Yang [15]:

$$\int_0^T \exp\left(\frac{-E_i}{RT}\right)dT = -\frac{E}{R}\frac{\exp(-x_i)}{x_i}h(x_i) \tag{5}$$

where $x_i = E_i/RT$, and $h(x_i)$ is given by the following expression:

$$h(x_i) = \frac{x_i^3+18x_i^2+88x_i+96}{x_i^4+20x_i^3+120x_i^2+240x_i+120} \tag{6}$$

From Eqs (4) and (5), we get:

$$\Sigma\lambda_i g_i(\alpha_i) = \sum \frac{\lambda_i A_i}{\beta} T \exp(-x_i)h(x_i) \tag{7}$$

Equations (1), (2) and (7) permit the simulation of solid-state processes constituted by a set of i independent reactions if both the kinetic equation and the kinetic parameters describing every unit reaction are assumed.

If it is taken into account [12] that solid-state reactions can be approximated to by n-order kinetic models, we can write

$$\Sigma\lambda_i \frac{\mathrm{d}\alpha_i}{\mathrm{d}t} = \Sigma\lambda_i Aa_i(1-\alpha_i)^{na_i} \exp(-xa_i) \tag{8}$$

This can be integrated, yielding

$$\Sigma\lambda_i \frac{1-(1-\alpha_i)^{1-na_i}}{1-na_i} = \sum \frac{\lambda_i Aa_i T}{\beta} \exp(-xa_i)h(xa_i) \tag{9}$$

where the subscript a refers to the apparen character of the parameters concerned. The integration of Eq. (8) for unit reactions fitting a first-order model (F1, A2 and A3 in Table 1) gives

$$\ln \frac{1}{1-\alpha_i} = \frac{Aa_i T}{\beta} \exp(-xa_i)h(xa_i) \tag{10}$$

$(na_i \neq 1)$

However, it must be pointed out that Eq. (9) can be generalized in order to fit first-order reactions as well. In fact, the error yielded in the α values obtained by simulating a first-order reaction with $n = 0.98$ is lower than 0.05%. This error decreases in proportion as n_i approaches 1.

By substituting the values of $(1-\alpha_i)$ given by Eq. (9) into Eq. (8), one gets the general equation that describes the overall process:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \Sigma\lambda_i Aa_i \exp(-xa_i)\left[1-(1-na_i)\frac{Aa_i T}{\beta}\exp(-xa_i)h(xa_i)\right]^{\frac{na_i}{1-na_i}} \tag{11}$$

The computer program for deconvolution

The calculation program is based on the Meiron algorithm

$$x_{m+1} = x_m - (B_m + PC_m)^{-1} G_m \tag{12}$$

where x_m is a vector that stores the input parameters for each independent reaction: Aa_i, Ea_i, na_i and λ_i. x_{m+1} stores the parameters calculated from x_m, which are used as starting parameters for the next iteration. B_m, C_m and G_m are two symmetric matrices and a vector, respectively, which store the difference between the overall rate and the one generated from the input parameters. The scalar P_i is a smoothing factor. The non-linear optimization procedure developed by Jones and Pitta [16] for deconvoluting Cauchy–Gauss-shaped overlapping curves has been modified so as to be appliable to traces described by Eq. (2). The maximum numbers of curves to be deconvoluted by the program is limited to 15.

The apparent kinetic parameters of the unit overlapping reactions have been optimized by minimizing the function R described as follows:

$$R=\sum\left[\left(\frac{d\alpha}{dt}\right)_{cal}-\left(\frac{d\alpha}{dt}\right)_{exp}\right]^2 \tag{13}$$

The computer program is stopped when the ratio R_m/R_{m-1} is 1.000002, m being the number of iterations.

Discrimination of reaction mechanisms and kinetic parameters of unit reactions

It has been shown in recent papers [17] that the method proposed by Kissinger for determination of the activation energies of homogeneous reactions can also be applied to heterogeneous reactions obeying the kinetic equations given in Table 1. Therefore, the activation energy can be calculated, without previous assumptions regarding the reaction mechanism, from the temperature of maximum reaction rate, T_m, determined at different heating rates from a series of non-isothermal experiments, according to the following equation:

$$\ln\frac{\beta}{T_m^2}=-\frac{E}{RT_m}+Cte \tag{14}$$

The slope of a plot of the left-hand side of Eq. (14) as a function of $1/T_m$ yields the activation energy. The activation energies of the independent reactions would be calculated from the peak temperatures of the deconvoluted DTG curves obtained from a series of experimental traces recorded at different heating rates. Once the real activation energies, E, are known, the kinetic models can be discriminated from the ratio E_a/E and the apparent reaction order *na.*

Results

Figure 1 shows the overall curves of a process constituted by three independent reactions simulated by means of Eqs (6) and (7) with the assumption of a heating rate of 6 deg/min and the kinetic models and kinetic parameters given in Table 2.

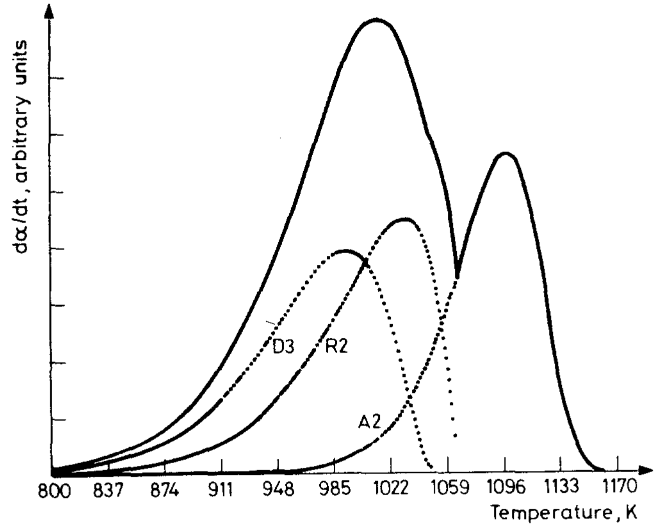

Fig. 1 Theoretical overall curves calculated assuming a heating rate $\beta = 6$ deg/min

Table 2 Results of deconvolution of three independent reactions

Mechanism	Theoretical values		Apparent values		
	E, kJ/mol	A, min^{-1}	E_a, kJ/mol	A_a, min^{-1}	n_a
A2(1)	167	$1\cdot10^{7}$	346	$6\cdot10^{15}$	0.983
D3(2)	334	$1\cdot10^{16}$	160	$3\cdot10^{7}$	0.668
R2(3)	176	$1\cdot10^{8}$	176	$1\cdot10^{8}$	0.500

The simulated curve in Fig. 1 was deconvoluted with the previously described computer program, using as starting input data one hundred points homogeneously distributed along the curve and the following kinetic parameters: $E_1 = E_2 = E_3 = 160$ kJ/mol; and $n_1 = n_2 = n_3 = 0.5$. The values of E and n were arbitrarily selected. However, the values of A were selected in such a way that the temperatures of the maximum reaction rate calculated from the starting kinetic parameters agree with the temperatures of the peaks and/or the shoulders of the simulated curves. This procedure approximates the curve calculated from the input data to the real one, minimizing the number of iterations required to achieve the best fitting. The following correlation between β, A, E and T_m at the maximum reaction rate (i.e. $d\alpha^2/dt^2 = 0$) is obtained.

$$A \approx \frac{E\beta}{RT_m^2}\exp\left(E/RT_m\right) \tag{15}$$

The overall $d\alpha/dt$ vs. T curve and the traces of the three unit reactions leading to the best fitting of the simulated curve in Fig. 1 are drawn in dotted lines in the same Figure. The apparent kinetic parameters calculated for the deconvoluted reactions are given in Table 2.

On the other hand, in order to check the method proposed for the discrimination of the mechanism of three mutually independent reactions, the series of DTG curves shown in Figs 2–5 were simulated using the kinetic parameters shown in Table 2, but different heating rates. The deconvoluted curves obtained after running the computer program described here are drawn in the same Figure. It is noteworthy that the calculated values of Ea, Aa and na agree with those given in Table 2.

The real activation energies were determined from the plots of the values of T_m taken from Figs 2 to 5 according to Eq. (14), as shown in Fig. 6. The results obtained are given in Table 3, together with the ratios E_a/E.

The above data demonstrate that the activation energies calculated with the Kissinger method show a very good agreement with the theoretical ones. Moreover, a comparison of the values determined for na and E_a/E with those reported in Table 1 leads to the conclusion that the unit reactions 1, 2 and 3 fit the kinetic models A_2, D_3 and R_3, respectively, as assumed for simulation of the curves.

To summarize, it can be concluded that both the activation energies and the kinetic model satisfied by a series of mutually independent overlapping reactions

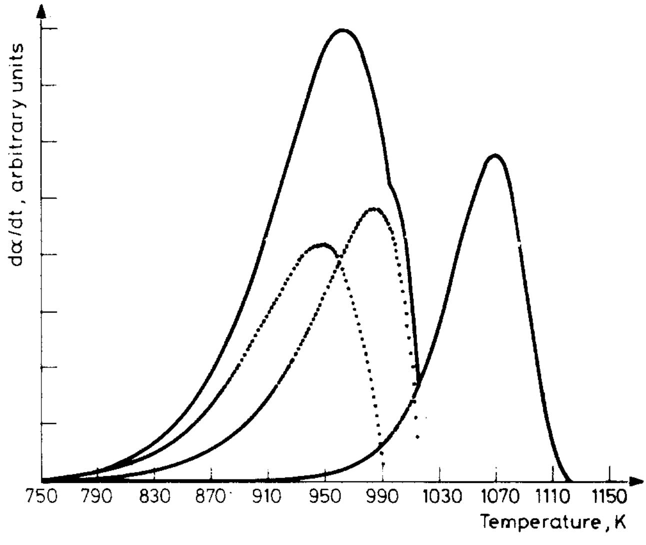

Fig. 2 Deconvolution of the overal $d\alpha/dt-T$ curve calculated assuming a heating rate $\beta=2$ deg/min

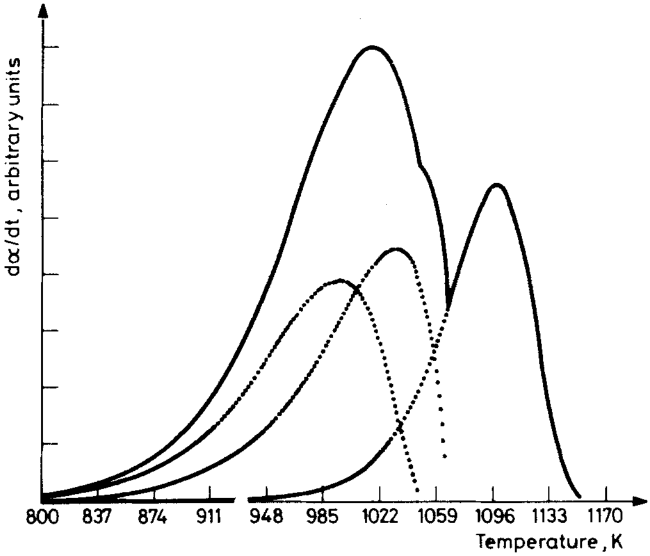

Fig. 3 Deconvolution of the overall dα/dt – T curve calculated assuming a heating rate $\beta = 6$ deg/min

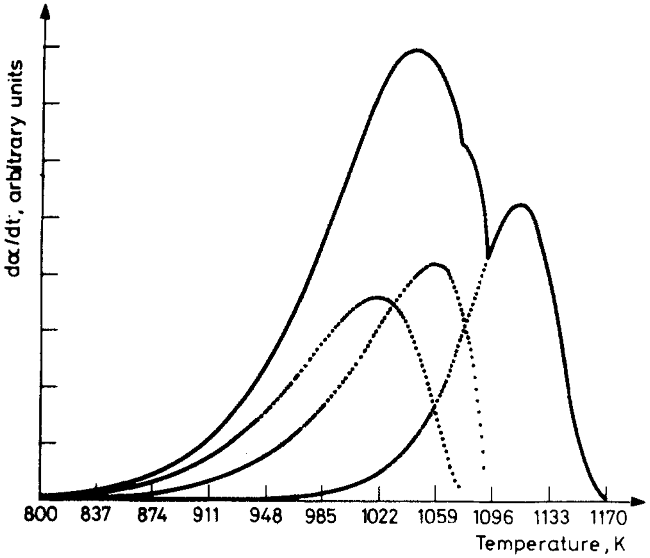

Fig. 4 Deconvolution of the overall dα/dt – T curve calculated assuming a heating rate $\beta = 10$ deg/min

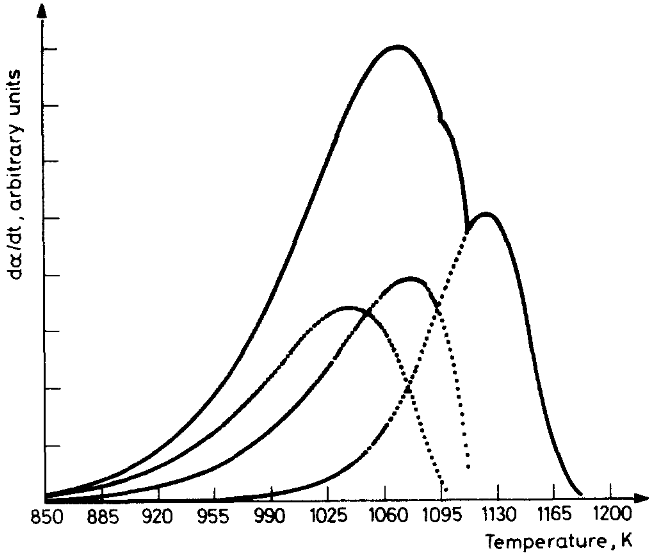

Fig. 5 Deconvolution of the overall dα/dt – T curve calculated assuming a heating rate $\beta = 15$ deg/min

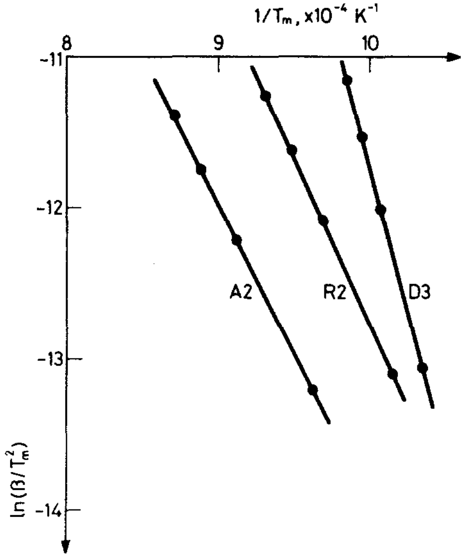

Fig. 6 Kissinger plots of the values of T_m taken from Figs 2 to 5

can be determined from a series of experimental DTG curves obtained at several heating rates by using the computer method outlined here. Once the kinetic model and the activation energies are known, the preexponential Arrhenius factor can be calculated from the kinetic analysis of the single deconvoluted curves by means of the equation:

$$\frac{d\alpha}{dt} = Af(\alpha)\exp(-E/RT) \tag{16}$$

after substitution of the proper expression of the $f(\alpha)$ function. The values of A obtained from the plot of ln $(d\alpha/dt)$ *vs.* $1/T$ are included in Table 3. They show good agreement with the theoretical ones.

Table 3 Discrimination of kinetic models with Kissinger's analysis

Mechanism	E, kJ/mol	A, min^{-1}	E_a/E	r
1(A2)	165	$2\cdot10^{7}$	2.08	0.99998
2(D3)	316	$8\cdot10^{15}$	0.50	0.99973
3(R2)	181	$9\cdot10^{7}$	0.98	0.99993

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Zusammenfassung — Es wurde eine methode zur Dekonvolution von bis zu 15 einander überlappenden Festphasenreaktionen entwickelt, die keinerlei vorherige Annahmen notwendig macht. Mittels einer Reihe nichtisothermer Experimente mit unterschiedlichen Aufheizgeschwindigkeiten können sowohl die kinetischen Parameter als auch der Reaktionsmechanismus der Teilreaktionen bestimmt werden.

Резюме — Разработан метод, позволяющий разделить перекрывающиеся твердотельные реакции с числом их до 15. Кинетические параметры и реакционный механизм каждой единичной реакции могут быть определены на основе ряда неизотермических измерений проведенных при различных скоростях нагрева.