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COMPUTER KINETIC ANALYSIS OF SIMULTANEOUSLY OBTAINED TG AND DTG CURVES

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The computer kinetic analysis of simultaneously obtained TG and DTG curves of $CaCO_3$ decomposition has been carried out. Ten different kinetic equations have been tested to decide the mechanism which drives the reaction. Either a two-thirds kinetic equation (phase boundary process) or a Jander equation (diffusion process) satisfactorily describe the kinetic data of both decomposition curves. From these results we conclude there is no chance of differentiating between these two mechanisms by only the kinetic analysis of TG and DTG curves separately.

A better approach to the problem is possible if the kinetic analysis is performed on simultaneous TG and DTG curves, together with an isothermal one. This procedure might be a valid way to establish the mechanisms of thermal decomposition reactions by means of kinetic methods without additional information.

We recently revewed the application of TG methods to establish the kinetics of thermal decomposition reactions of solids [1–2]. It was concluded that TG curves of any reaction, following either diffusion kinetics or Avrami–Erofeev or Prout–Tompkins mechanisms, necessarily fit some of the integral kinetic equations available for "n-order reactions". Then, it is not possible to determine the mechanism of a solid-state reaction from TG curves alone.

However, it is necessary to point out that different integral kinetic equations usually fit the same experimental TG curve. This fact does not imply that the mathematical transformations of such integral equations e.g. differential and differential-differential forms, fit the corresponding transformations of the TG curves i.e. the DTG or DDTG curves. Only if the selected kinetic equation correctly described the course of the reaction mechanism must the kinetic parameters calculated from both the TG curve and any of its transformations coincide.

The present paper attempts to explore the advantages of simultaneous kinetic analysis of both a TG curve and one of its mathematical transformations in order to determine the mechanisms of thermal decomposition reactions of solids by kinetic methods without additional information. The thermal decomposition of $CaCO_3$ was selected as test reaction since its mechanism has been well established [3]. With this in mind, the kinetic analysis of a TG curve and its corresponding DTG curve was performed, some of the most frequently mechanisms proposed in the literature for the thermal decompositions of solids being assumed. A comparative study of the kinetic parameters obtained from the two curves might clear up the mechanism of the process.

Experimental

The samples of $CaCO_3$ were D'Hemio, r.a. Thermogravimetric analysis was carried out on a Cahn Electrobalance, model RG. Samples (50 mg) were heated under vacuum (ca. 10^{-4} Torr) at a heating rate of 12°/min. The temperature was measured with a chromel-alumel thermocouple placed outside the balance tube, as near as possible to the sample.

Results and discussion

The TG and DTG curves for a sample of $CaCO_3$ are presented in Fig. 1.

Kinetic analysis of the DTG curve was performed by means of the method due to Achar et al. [4]. The following equation was used to obtain the kinetic parameters:

$$\ln \frac{(\mathrm{d}\alpha/\mathrm{d}T}{f(\alpha)} = \ln \frac{A}{\beta} - \frac{E}{RT}\,. \tag{1}$$

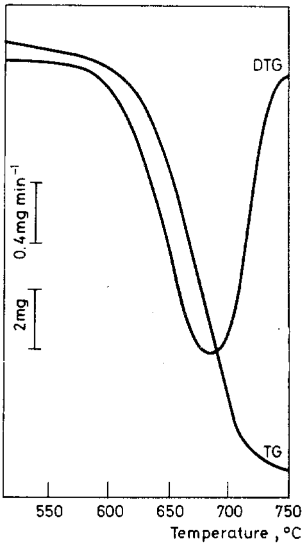

Fig. 1. TG and DTG curves of $CaCO_3$ thermal decomposition under vacuum.
$\beta = 12°/\mathrm{min}$

When the selected function, $f(\alpha)$, fits the experimental data, the plot of the left-hand side of Eq. (1) *vs.* $1/T$ results in a straight line from which the activation energy E, and the frequency factor, A, can be determined.

The TG curve was analyzed by the Coats and Redfern method [5], using the equation:

$$\ln g(\alpha) - 2 \ln T = \ln \frac{AR}{E\beta} - \frac{E}{RT}. \tag{2}$$

The kinetic parameters of decomposition reactions can be obtained from this equation by applying the same analytical procedure as used in Eq. (1).

When the kinetics of decomposition are interpreted in terms of an Avrami mechanism, Eq. (2) becomes:

$$\ln \ln \frac{1}{1-\alpha} - 2p \ln T = \ln \frac{pRA^{1/p}}{E\beta} - \frac{E}{RT} \tag{3}$$

where p is a constant related with the growth of the nuclei.

Table 1

Algebraic expressions of differential, $f(\alpha)$, and integral, $g(\alpha)$, functions for the most common mechanisms operating in solid-state decompositions

Symbol	$f(\alpha)$	$g(\alpha)$	Mechanism
R_1	1	α	Zero-order mechanism. Polany—Wigner equation.
R_2	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$	One-half order mechanism.
R_3	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$	Two-thirds order mechanism.
F_1	$(1-\alpha)$	$-\ln(1-\alpha)$	First-order mechanism.
A_2	$2[-\ln(1-\alpha)^{1/2}](1-\alpha)$	$[-\ln(1-\alpha)]^{1/2}$	Two-dimensional growth of nuclei. Avrami equation.
A_3	$3[-\ln(1-\alpha)^{2/3}](1-\alpha)$	$[-\ln(1-\alpha)]^{1/3}$	Three-dimensional growth of nuclei. Avrami equation.
D_1	$1/2\alpha$	α^2	One-dimensional diffusion.
D_2	$1/[-\ln(1-\alpha)]$	$(1-\alpha)\ln(1-\alpha) + \alpha$	Two-dimensional diffusion.
D_3	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{1/3}]$	$[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion. Jander equation.
D_4	$3/2[(1-\alpha)^{-1/3}-1]$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	Three-dimensional diffusion. Ginstling—Brounshtein equation.

The algebraic expressions for the $f(\alpha)$ and $g(\alpha)$ functions corresponding to the mechanisms more commonly used in the literature for the thermal decomposition reactions of solids are given in Table 1.

For kinetic analysis of the TG and DTG data, a program in Fortran IV was developed. This program allows one to establish the kinetic parameters of the reaction from each function listed in Table 1, and the respective linear regression coefficients.

The results obtained from analysis of the TG and DTG curves of Fig. 1 in the range of conversion fraction $0.2 < \alpha < 0.9$ are listed in Table 2. We can see that when the experimental data are analyzed by considering that the thermal decomposition of $CaCO_3$ is described by the mechanisms R_2, F_1, A_2, D_1, D_2, D_3 and D_4, the kinetic parameters obtained from eqs. (1), (2) and (3) are different. Only the mechanisms R_3 and D_3 lead to an agreement between the kinetic parameters by both integral and differential methods. On the other hand, it has been demonstrated in a previous paper [1] that TG data of 2/3-order reactions also fit the kinetic equation for a Jander diffusion mechanism, namely D_3, giving an activation energy twice the value corresponding to the R_3 process. Conversely, if a reaction follows mechanism D_3 giving an activation energy E, a value of $E/2$ would be obtained assuming that the reaction takes place through mechanism R_3. As shown in Table 2, the ratio between the activation energies calculated assuming mechanisms D_3 and R_3 lies very close to 2, in good agreement with the earlier considerations.

Table 2

Numerical data obtained by computer, resulting from the analysis of the curves in Figure 1 by different kinetic mechanisms

Mechanism	Integral method			Differential method		
	E_a, kcal mole^{-1}	A, min^{-1}	Regression coefficient	E_a, kcal mole^{-1}	A, min^{-1}	Regression coefficient
R_1	33.2	$5.6 \cdot 10^6$	−0.98463	11.6	$5.7 \cdot 10^1$	−0.76687
R_2	42.5	$1.2 \cdot 10^9$	−0.99402	36.1	$4.2 \cdot 10^7$	−0.99163
R_3	46.0	$9.0 \cdot 10^9$	−0.99606	44.3	$3.8 \cdot 10^9$	−0.99760
F_1	53.8	$7.4 \cdot 10^{11}$	−0.99871	60.6	$3.1 \cdot 10^{13}$	−0.99985
A_2	50.0	$7.8 \cdot 10^9$	−0.99849	63.8	$1.6 \cdot 10^{13}$	−0.99850
A_3	46.2	$4.2 \cdot 10^7$	−0.93331	66.9	$4.8 \cdot 10^{12}$	−0.99546
D_1	70.3	$2.2 \cdot 10^{15}$	−0.98627	48.6	$2.1 \cdot 10^{10}$	−0.95272
D_2	81.4	$6.3 \cdot 10^{17}$	−0.99175	69.0	$8.6 \cdot 10^{14}$	−0.98483
D_3	95.8	$4.5 \cdot 10^{20}$	−0.99639	94.0	$1.8 \cdot 10^{20}$	−0.99718
D_4	86.2	$2.0 \cdot 10^{18}$	−0.99364	77.7	$2.2 \cdot 10^{16}$	−0.99128

To summarize, the results reported in the present paper seem to indicate rather clearly that both TG and DTG curves of a sample of $CaCO_3$ can only be described either by a two-thirds order reaction or a Jander diffusion mechanism, but it is not possible to distinguish between these two mechanisms by TG or DTG. The valuable assistance provided by differential methods of thermogravimetric data, as suggested by Sestak et al. [6], is not evident. Certainly, both integral and differential forms of the function given in Table 1 are analytically distinguishable, but as the kinetic methods more frequently used in the literature to evaluate kinetic parameters imply linearization of the thermogravimetric curves, it is necessary to compare the logarithmic forms of the functions.

As regards the Jander (D_3) and contracting sphere (R_3) mechanisms a comparative study is further elaborated. On subtraction of Eq. (1) for both mechanisms, the following equation results:

$$\ln \frac{f_{R_3}(\alpha)}{f_{D_3}(\alpha)} = \ln \frac{A_{D_3}}{A_{R_3}} - \frac{E_{D_3} - E_{R_3}}{RT}\,. \tag{4}$$

Taking into account the algebraic expressions for $f_{R_3}(\alpha)$ and $f_{D_3}(\alpha)$ given in Table 1, expression (4) becomes:

$$\ln\,[1 - (1 - \alpha)^{1/3}] = \ln \frac{3A_{D_3}}{2A_{R_3}} - \frac{E_{D_3} - E_{R_3}}{RT}\,. \tag{5}$$

As the algebraic expression of the left-hand side of Eq. (5) corresponds with the integral form of function R_3 (see Table 1), the activation energy obtained from this equation would be very close to E_{R_3}. Hence, approximately,

$$E_{D_3} \approx 2E_{R_3}\,.$$

Therefore, it is evident that those data on solid thermal decompositions which can be described by a Jander mechanism must also fit a two-thirds order kinetic

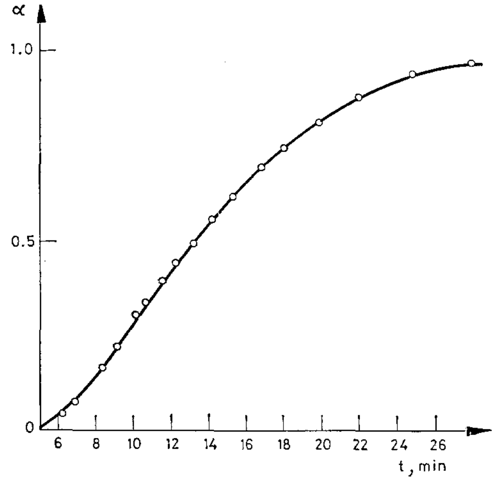

Fig. 2. Isothermal run on the decomposition of $CaCO_3$ at 660°

equation and vice versa, whether a TG or a DTG curve is used. The extension of this comparative study to other mechanisms will be reported in detail elsewhere [7].

However, if we take into account that $g(\alpha)$ functions of mechanisms R_3 and D_3 in Table 1 are not linearly correlated, it would be possible to distinguish between these two mechanisms from an isothermal α *vs.* t curve, plotting the $g(\alpha)$ function against t.

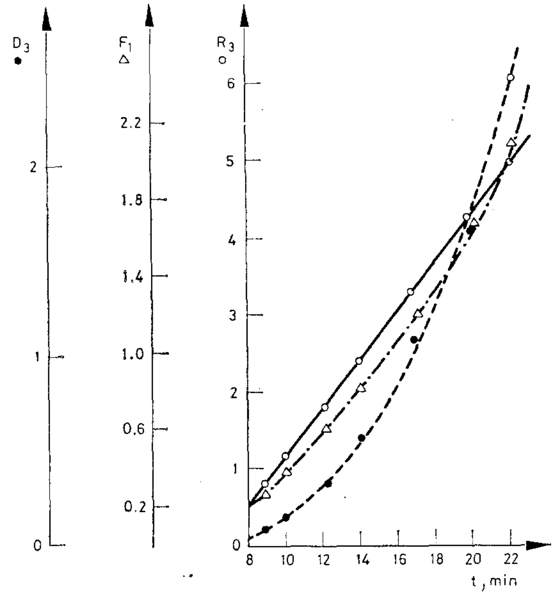

Fig. 3. Tests on data from Fig. 1 for R_3, D_3 and F_1 mechanisms. Range of $\alpha = 0.2-0.9$

An isothermal curve of $CaCO_3$, obtained at 660°, is given in Fig. 2. The values of $g(\alpha)$ calculated for the D_3 and R_3 functions *vs.* time are shown in Fig. 3. We can see that only the R_3 function exhibits a good linear correlation with time ($r = 0.9995$). Therefore, the reaction does not follow a D_3 mechanism but is controlled by an interface mechanism R_3.

The above considerations allow the conclusion that the simultaneous analysis of both a TG and a DTG diagram and a single isotherm curve makes it possible to establish the mechanism of a thermal decomposition reaction merely via a kinetic method, without any additional information.

On the other hand, the data of Table 2 show that the criterion for deciding the most probable mechanism based on the better linear regression coefficient would lead to a meaningless conclusion. In fact, a higher regression coefficient was obtained for a first-order reaction, in spite of the poor agreement between the kinetic parameters obtained the TG and DTG curves of Fig. 1 (see Table 2). Furthermore, the values calculated for the function F_1 from the isotherm of Fig. 2 do not show a good linear correlation with time, as can be seen in Fig. 3.

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Résumé — L'analyse cinétique des courbes TG et TGD obtenues simultanément lors de la décomposition de $CaCO_3$ a été effectuée à l'aide d'un ordinateur. Dix équations cinétiques différentes ont été examinées pour établir le mécanisme moteur de la réaction. L'équation cinétique de type 2/3 (processus d'interface) ou l'équation de Jander (processus de diffusion) décrivent toutes deux de manière satisfaisante les données cinétiques déduites des courbes TG et TGD. De ces résultats on conclut qu'il n'est pas possible de distinguer ces deux mécanismes en s'appuyant exclusivement sur l'analyse cinétique des courbes TG et TGD.

Une meilleure approche du problême est possible si l'on effectue l'analyse cinétique des courbes TG et TGD simultanées en même temps que celle d'une courbe isotherme. Ce procédé peut être un bon moyen pour élucider le mécanisme des réactions de décomposition thermique à l'aide de méthodes cinétiques, sans informations supplémentaires.

Zusammenfassung — Es wurde die kinetische Analyse simultan erhaltener TG- und DTG-Kurven der Zersetzung von $CaCO_3$ mittels Computer durchgeführt. Zehn verschiedene kinetische Gleichungen wurden zur Ermittlung des reaktionssteuernden Mechanismus erprobt. Die kinetischen Daten beider Zersetzungskurven können entweder durch eine "Zwei-Drittel" kinetische Gleichung (Phasen-Grenzflächenprozess) oder eine Jander-Gleichung (Diffusionsprozess) befriedigend beschrieben werden. Aus diesen Ergebnissen wird gefolgert, dass keine Möglichkeit besteht diese beiden Mechanismen ausschliesslich durch die kinetische Analyse der TG- und DTG-Kurven von einander zu unterscheiden. Eine bessere Annäherung an das Problem ist durch die kinetische Analyse simultaner TG- und DTG-Kurven gemeinsam mit einer isothermen Kurve möglich. Dieser Vorgang erscheint als ein möglicher Weg zur Unterscheidung der Mechanismen thermischer Zetsetzungsreaktionen an Hand kinetischer Methoden ohne Zusatzliche Information.

Резюме — С помощью ЭВМ был проведен кинетический анализ одновременно полученных ТГ и ДТГ кривых разложения карбоната кальция. Для установления механизма реакции были апробированы десять различных кинетических уравнений. Кинетические данные обоих кривых разложения удовлетворительно описываются как кинетическим уравнением второго-третьего порядка (процесс фазовой границы), так и уравнением Джендера (диффузионный процесс). Установить различия между этими двумя механизмами только на основе кинетического анализа ТГ и ДТГ кривых не представляется возможным. Для лучшего решения этой проблемы является проведение кинетического анализа кривых ТГ и ДТГ совместно с каким-либо изотермическим методом. Такой подход может быть более правильным для решения механизма реакций термического разложения с помощью кинетических методов без привлечения дополнительной информации.