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APPLICABILITY OF THE MASTER PLOTS IN KINETIC ANALYSIS OF NON-ISOTHERMAL DATA

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ABSTRACT

The ability to determine the actual reaction mechanism (RM) of solid state processes from a single non-isothermal curve was analysed and discussed. Owing to the correlation of all kinetic parameters the RM cannot be ascertained without the knowledge of activation energy. However, if the activation energy is known a simple and precise method for the determination of RM can be proposed.

The method was used to analyse the experimental data of the thermal decomposition of magnesium carbonate in vacuum. It was found that the reaction follows the R3 mechanism which is in very good agreement with the results of isothermal experiments.

INTRODUCTION

Several attempts have been made to determine the mechanism of a solid state process from one non-isothermal trace. Many studies which have evaluated experimental data have employed reference theoretical curves that are often called ‘master plots’ [1–4]. The master plot in this sense is a characteristic curve independent of the condition of the measurement which is easily obtained from experimental data.

In this paper we discuss the applicability of the master plots based on both the second and first derivatives of the reacted fraction α in a hypothetical reaction. The application of the method to the decomposition kinetics of magnesium carbonate is shown and discussed.

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THEORETICAL

Master plots based on the second derivative of α

The reaction rate of a solid state process can be described by the well-known general kinetic law

$$\mathrm{d}\alpha/\mathrm{d}t = A\ \mathrm{e}^{-x}\mathrm{f}(\alpha) \tag{1}$$

where $x = E/RT$ and $\mathrm{f}(\alpha)$ is an algebraic function depending on the mechanism of the process. If the temperature rises at a constant rate ($\beta = \mathrm{d}T/\mathrm{d}t$), eqn. (1) can be integrated and we obtain

$$\mathrm{g}(\alpha) = \frac{AE}{\beta R}\ \mathrm{e}^{-x}\left[\frac{\pi(x)}{x}\right] \tag{2}$$

It is known [5] that the function $\pi(x)$ is an approximation of the temperature integral which cannot be expressed in a simple analytical form. In this study we used the fourth rational expression of Senum and Yang [6] which gives errors of lower than $10^{-5}\%$ for $x = 20$

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

We can define the function characteristic for a particular kinetic model in the following way

$$\mathrm{w}(\alpha) = \frac{\mathrm{d}^2\alpha/\mathrm{d}t^2}{(\mathrm{d}\alpha/\mathrm{d}t)^2} \tag{4}$$

This function can serve as a master plot because it is independent of the heating rate and its values can easily be calculated from the experimental data. The general expression of $\mathrm{w}(\alpha)$ can be obtained by combining eqns. (1), (2) and (4), i.e.

$$\mathrm{w}(\alpha) = \frac{1}{\mathrm{f}(\alpha)}\left[\mathrm{f}'(\alpha) + \frac{x\pi(x)}{\mathrm{g}(\alpha)}\right] \tag{5}$$

It is evident that this function is also dependent on the value of x. In order to show the sensitivity of $\mathrm{w}(\alpha)$ to x we can discuss the problem for $\mathrm{w}(\alpha) = 0$. In this case it follows from eqn. (5)

$$-\mathrm{f}'(\alpha_\mathrm{m})\mathrm{g}(\alpha_\mathrm{m}) = x_\mathrm{m}\pi(x_\mathrm{m}) \tag{6}$$

where the subscript m is related to the maximum of $\mathrm{d}\alpha/\mathrm{d}t$. The algebraic expressions for the $\mathrm{f}(\alpha)$, $\mathrm{f}'(\alpha)$ and $\mathrm{g}(\alpha)$ functions are summarized in Table 1 and the dependences $\alpha_\mathrm{m}(x_\mathrm{m})$ are plotted in Fig. 1. The arrows at the right-hand side of this figure show the limiting values α_m^∞ for infinite x_m.

It can be seen that $\alpha_\mathrm{m}(x_\mathrm{m})$ functions decrease very rapidly for $x_\mathrm{m} < 20$ and they cross at various points. Under these circumstances it is very

TABLE 1

Algebraic expressions for the $f(\alpha)$, $f'(\alpha)$ and $g(\alpha)$ functions and the values of α_m^∞ for the most frequently used mechanisms of solid state processes

Model	$f(\alpha)$	$f'(\alpha)$	$g(\alpha)$	α_m^∞
An	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$	$(n-1)[-\ln(1-\alpha)]^{-1/n}-n[-\ln(1-\alpha)]^{1-1/n}$	$[-\ln(1-\alpha)]^{1/n}$	0.633
R$(1/(1-n))$	$(1-\alpha)^n$	$-n(1-\alpha)^{n-1}$	$\frac{1-(1-\alpha)^{1-n}}{1-n}$	$1-n^{1/(1-n)}$
D1	$\frac{1}{2}\alpha$	$-\frac{1}{2}\alpha^2$	α^2	1
D2	$\frac{1}{-\ln(1-\alpha)}$	$\frac{-1}{[\ln(1-\alpha)]^2(1-\alpha)}$	$(1-\alpha)\ln(1-\alpha)+\alpha$	0.834
D3	$\frac{3(1-\alpha)^{2/3}}{2\left[1-(1-\alpha)^{1/3}\right]}$	$\frac{1/2-(1-\alpha)^{-1/3}}{\left[1-(1-\alpha)^{1/3}\right]^2}$	$[1-(1-\alpha)^{1/3}]^2$	0.704
D4	$\frac{3}{2\left[(1-\alpha)^{-1/3}-1\right]}$	$\frac{-(1-\alpha)^{-4/3}}{2\left[(1-\alpha)^{-1/3}-1\right]^2}$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	0.776

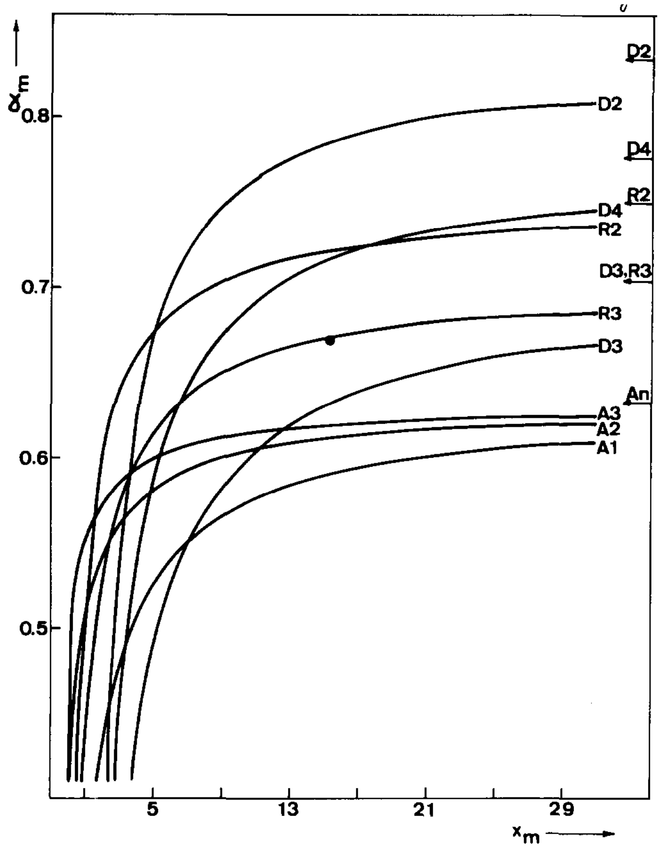

Fig. 1. The dependences of $\alpha_m(x_m)$ for the kinetic models discussed. The limiting values of α_m^∞ are shown by arrows. Experimental point (●).

difficult to draw any conclusions about the kinetic models without the precise knowledge of x_m. The differences between several kinetic models become smaller for $x_m > 20$, and for infinite x_m it is not possible to distinguish between D2, D3 and A*n* models.

Identical results are obtained for a hyperbolic heating schedule, i.e. $T = 1/(t_0 - bt)$, because it can be shown that this corresponds to linear heating when x is infinite, for which

$$\lim_{x \to \infty} x\pi(x) = 1 \tag{7}$$

Equation (5) can be rewritten for hyperbolic heating to give

$$\mathrm{w}(\alpha) = \frac{1}{\mathrm{f}(\alpha)}\left[\mathrm{f}'(\alpha) + \frac{1}{\mathrm{g}(\alpha)}\right] \tag{8}$$

The master curves corresponding to eqn. (8) are plotted in Fig. 2. It is evident that it is not possible to distinguish between D1 and R1 mecha-

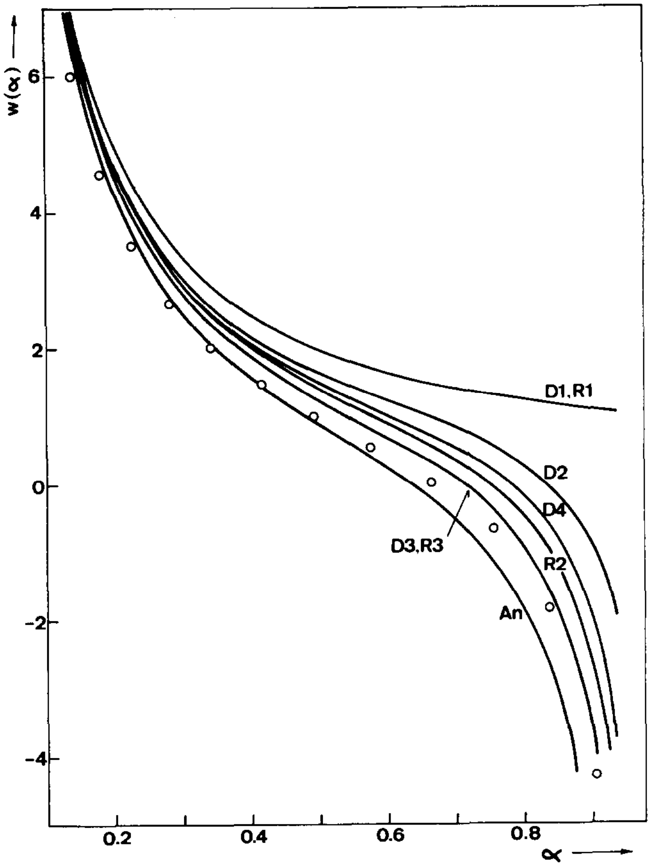

Fig. 2. The master curves w(α). Experimental data transformed by eqn. (4).(o).

nisms. Similarly there is no difference between mechanisms D3 and R3. Equation (8) can be written for the An kinetic model in the form

$$w(\alpha) = \frac{1 - \ln(1 - \alpha)}{(1 - \alpha) - \ln(1 - \alpha)} \tag{9}$$

which does not depend on the value of parameter n. Thus corresponding master curves are identical for this model, regardless of the value of the kinetic exponent n.

Master plots based on the first derivative of α

Recently [4], the master equation based on the first derivative of α has been derived in the form

$$y(\alpha) = \left(\frac{T}{T_{0.5}}\right)^2 \frac{(\mathrm{d}\alpha/\mathrm{d}t)}{(\mathrm{d}\alpha/\mathrm{d}t)_{0.5}} \tag{10}$$

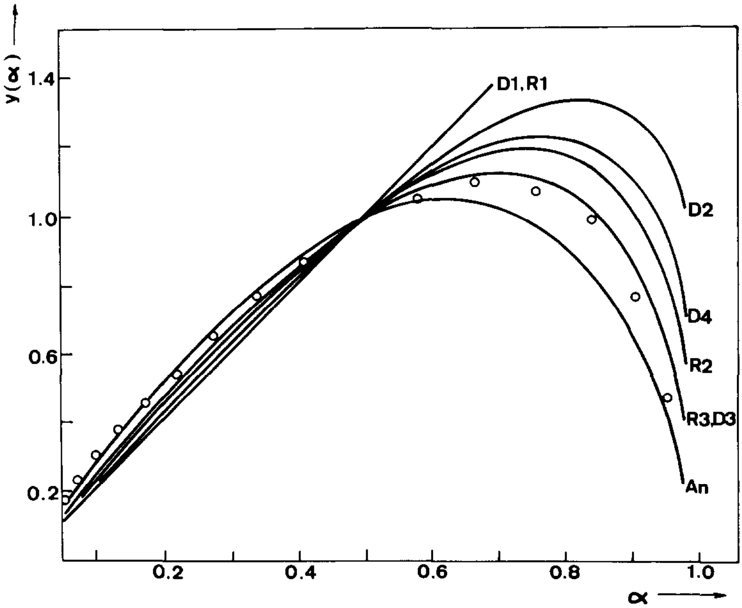

Fig. 3. The master curves y(α). Experimental data transformed by eqn. (10) (o).

where $T_{0.5}$ and $(d\alpha/dt)_{0.5}$ are the temperature and the rate respectively when $\alpha = 0.5$. It can easily be shown [4], that for the function y(α) another expression exists, i.e.

$$y(\alpha) = \frac{f(\alpha) \cdot g(\alpha)}{f(0.5) \cdot g(0.5)} \tag{11}$$

The master curves corresponding to eqn. (11) are plotted in Fig. 3. However, the results are very similar to those of the w(α) function and again it is impossible to distinguish between certain mechanisms (as described above for w(α)). This conclusion is not surprising because eqns. (10) and (11) are equal only for hyperbolic heating or for infinite x in the case of a linear heating programme. Thus it seems that unless the activation energy is known a priori it is impossible to ascertain the reaction mechanism, even for a hyperbolic heating schedule.

However, it has previously been demonstrated [7] that the activation energy of a solid state reaction can be determined from several non-isothermal measurements whatever the reaction mechanism. If the value of the activation energy is known the kinetic model of the process can be found in the following way. We can define the function

$$z(\alpha) = \frac{(d\alpha/dt)}{\beta} \pi(x) T \tag{12}$$

and then from eqns. (1) and (2) we obtain

$$z(\alpha) = f(\alpha) \cdot g(\alpha) \tag{13}$$

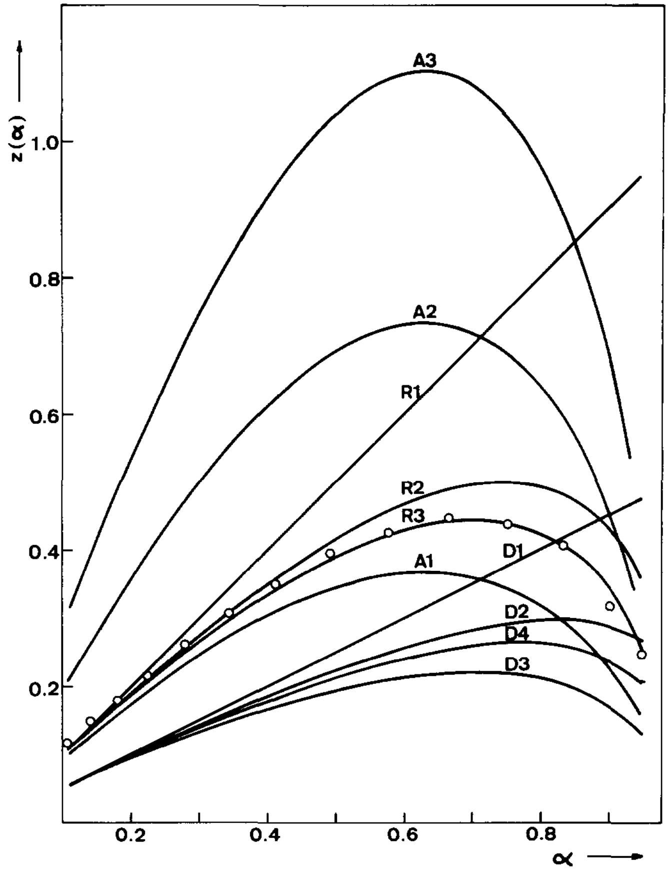

Fig. 4. The master curves z(α). Experimental data transformed by eqn. (12) (o).

The master plots corresponding to eqn. (13) are shown in Fig. 4. It can be seen that in this case all curves corresponding to all the models discussed are well separated. The master curves attain their maxima when the degree of conversion reaches its characteristic value. It can simply be shown that for the maximum of the z(α) function a general condition exists of the form

$$-f'(\alpha_m^\infty)\cdot g(\alpha_m^\infty)=1 \tag{14}$$

The values of α_m^∞ calculated from eqn. (14) are summarized in Table 1. All these properties of the z(α) functions are very useful for the determination of the kinetic model from non-isothermal experimental data. Thus by plotting the z(α) function calculated according to eqn. (12) and comparing with Fig. 4 we can determine easily and precisely the proper kinetic model.

EXPERIMENTAL

Magnesite from Navarra (Spain) was used for the experiment. This

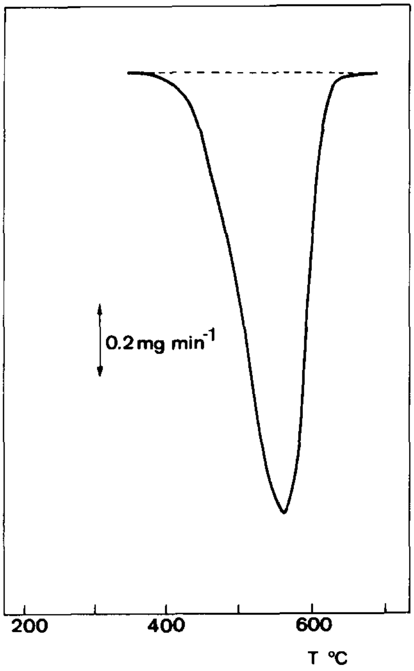

Fig. 5. DTG curve of the decomposition of $MgCO_3$ in vacuum at a heating rate of 12 K min^{-1}.

carbonate exhibits the following chemical composition: SiO_2, 1.76%; Fe_2O_3, 1.12%; Al_2O_3, 0.32%; CaO, 0.98%; MgO, 45.35%; loss of ignition, 50.50%.

The thermogravimetric run was carried out in a vacuum of 0.13 Pa using a CAHN electrobalance model RG. The Stanton-Redcroft temperature controller held the temperature constant to within ± 1 K. The mass of the sample and the heating rate were 11.1 mg and 12 K min^{-1} respectively.

RESULTS AND DISCUSSION

The DTG curve of the decomposition of $MgCO_3$ in vacuum [8] is shown in Fig. 5. It is supposed that the activation energy has a value E of 107 kJ mol^{-1} which has been confirmed by isothermal experiments. The values of the $z(\alpha)$ function calculated using eqn. (12) are plotted in Fig. 4 (open circles) for our experimental data. It is clear that the experimental data fit the master curve of the R3 mechanism very well. This conclusion is in very good agreement with the results of the analysis of isothermal data [8].

As another very quick test of the applicability of this particular kinetic model we can refer to Fig. 1. Our experimental data are $x_m = 13.4$ and $\alpha_m = 0.66$. From a simple visual inspection (filled circle) of Fig. 1 it can be seen that these values correspond well to the R3 model.

The experimental data given in Fig. 5 were also transformed using eqns. (4) and (10) respectively to obtain w(α) and y(α) functions. These characteristic dependences (open circles) are compared with their master plots in Figs. 2 and 3 respectively. The agreement between the master plots and the experimental data points is not so good as that obtained for the z(α) function.

Thus it can be concluded that the f(α) function cannot be ascertained from non-isothermal data obtained at only one heating rate unless the value of the activation energy is known. Nevertheless, the mechanism of the solid state process can easily be obtained by the simple method described above for a given value of activation energy.

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