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Note

Kinetic analysis of DTG data from master curves

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The aim of the present note is to develop a series of master curves for an easy and quick analysis of the mechanism of thermal decomposition reaction of solids from DTG data.

It is well known[1] that the reaction rate of the above named reactions is given by the equation:

$$\frac{d\alpha}{dt} = A \cdot e^{-E/RT} \cdot f(\alpha) \tag{1}$$

where α is the reacted fraction; t, the time; $f(\alpha)$ a function depending on the reaction mechanism; A, the pre-exponential factor of Arrhenius; E, the activation energy; R, the gas constant and T, the absolute temperature.

If the temperature of the sample increases at a constant rate, β, eqn (1) can be integrated[2] and becomes:

$$g(\alpha) = \frac{ART^2}{E\beta} \cdot e^{-E/RT} \tag{2}$$

From eqns (1) and (2), we obtain:

$$g(\alpha) = \frac{RT^2}{E\beta} \frac{d\alpha}{dt} \frac{1}{f(\alpha)} \tag{3}$$

which for $\alpha = 0.5$ becomes:

$$g(0.5) = \frac{RT_{0.5}^2}{E\beta} \left(\frac{d\alpha}{dt}\right)_{0.5} \frac{1}{f(0.5)} \tag{4}$$

where $T_{0.5}$ and $(d\alpha/dt)_{0.5}$ are, respectively, the temperature and the rate when $\alpha = 0.5$.

From eqns (3) and (4), it is very easy to obtain:

$$\left(\frac{T}{T_{0.5}}\right)^2 \frac{(d\alpha/dt)}{(d\alpha/dt)_{0.5}} = a \cdot f(\alpha) \cdot g(\alpha) \tag{5}$$

where $a[= 1/f(0.5) \cdot g(0.5)]$ is a constant for a given mechanism.

TABLE 1

ALGEBRAIC EXPRESSIONS OF THE FUNCTIONS $f(\alpha)$, $g(\alpha)$ AND "REDUCED RATE"

Symbol[a]	$g(\alpha)$	$f(\alpha)$	*Reduced rate* $(T/T_{0.5})^2 \cdot (d\alpha/dt)/(d\alpha/dt)_{0.5}$
R_1	α	1	2α
R_2	$2[1-(1-\alpha)^{1/2}]$	$(1-\alpha)^{1/2}$	$4.8284\,[(1-\alpha)^{1/2}-(1-\alpha)]$
R_3	$3\,[1-(1-\alpha)^{1/3}]$	$(1-\alpha)^{2/3}$	$7.6946\,[(1-\alpha)^{2/3}-(1-\alpha)]$
$F_1(\alpha)$	$\ln(1-\alpha)$	$(1-\alpha)$	$-2.8854\,(1-\alpha)\ln(1-\alpha)$
D_1	α^2	$1/2\alpha$	2α
D_2	$(1-\alpha)\ln(1-\alpha)+\alpha$	$-\dfrac{1}{\ln(1-\alpha)}$	$-4.5178\left[(1-\alpha)+\dfrac{\alpha}{\ln(1-\alpha)}\right]$
D_3	$[1-(1-\alpha)^{1/3}]^2$	$\dfrac{3}{2}\,\dfrac{(1-\alpha)^{2/3}}{1-(1-\alpha)^{1/3}}$	$7.6946\,[(1-\alpha)^{2/3}-(1-\alpha)]$
D_4	$\left(1-\dfrac{2\alpha}{3}\right)-(1-\alpha)^{2/3}$	$\dfrac{3}{2}\,\dfrac{1}{(1-\alpha)^{-1/3}-1}$	$7.0811\left[\left(1-\dfrac{2\alpha}{3}\right)-(1-\alpha)^{2/3}\right]\dfrac{1}{(1-\alpha)^{-1/3}-1}$
A_2	$[-\ln(1-\alpha)]^{1/2}$	$2\,[-\ln(1-\alpha)^{1/2}](1-\alpha)$	$-2.8854\,(1-\alpha)\ln(1-\alpha)$
A_3	$[-\ln(1-\alpha)]^{1/3}$	$3\,[-\ln(1-\alpha)^{2/3}](1-\alpha)$	$-2.8854\,(1-\alpha)\ln(1-\alpha)$

[a] The symbols of Sharp et al.[5] have been used.

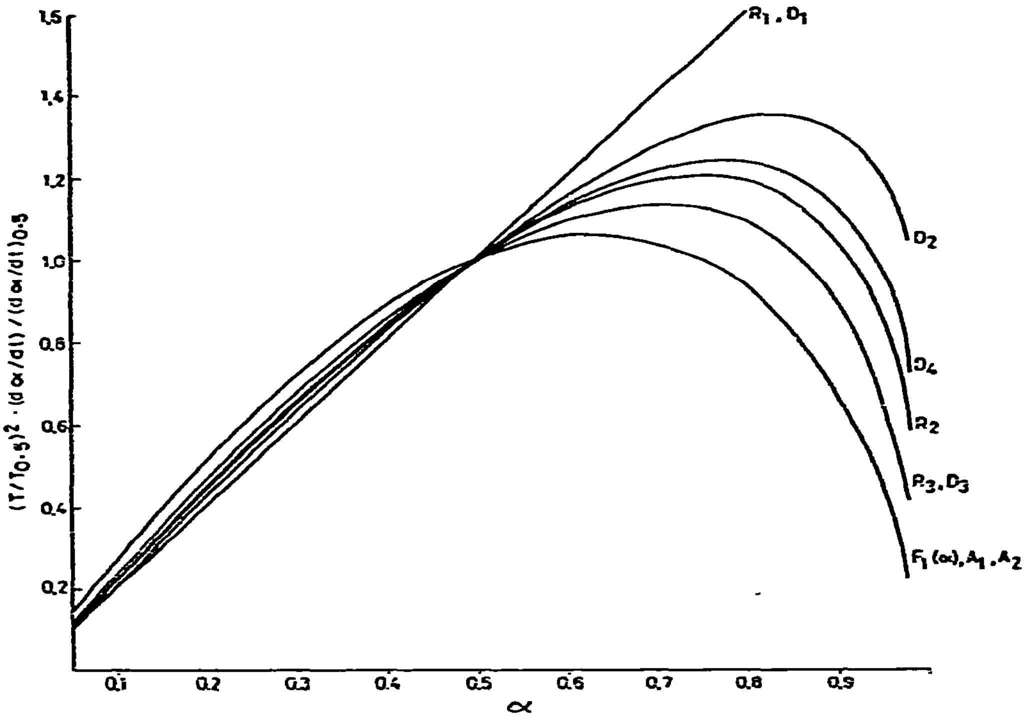

Fig. 1. Reduced rate–α master curves of different reaction mechanisms of thermal decomposition of solids.

If we consider that $T/T_{0.5}$ is close to unity, eqn. (5) shows that the plot of "reduced rate" [i.e., $(d\alpha/dt)/(d\alpha/dt)_{0.5}$] against α gives a series of master curves that depend neither on the kinetic parameters nor on the heating rate but only on the reaction mechanism.

The equations of the master curves obtained are included in Table 1 and plotted in Fig. 1. We can see that it is not possible to distinguish between the mechanism R_3 and D_3 (see the nomenclature in Table 1). On the other hand, it is impossible to discern between a first-order reaction and the Avrami-Erofeev mechanism by means of these curves. A similar conclusion was reached by analyzing TG data in a prior publication[3].

The method developed in the present work has the advantage of allowing the quick selection of a single mechanism or, in the worst case, a small group of them. In this way, the work required for performing the kinetic analysis and to determine the activation energy of the reaction is considerably shortened.

In order to check the master curves, the DTG diagram of $CaCO_3$ obtained under vacuum[4] and included in Fig. 2 has been analyzed. The values of $(T/T_{0.5})^2$ $[(d\alpha/dt)/(d\alpha/dt)_{0.5}]$ calculated from Fig. 2 are plotted versus α in Fig. 3. We can see that the experimental data fit very well the master curve of the R_3 mechanism, in good agreement with the conclusion previously reached[3] from the analysis of isothermal and TG data of the thermal decomposition of the same sample of $CaCO_3$

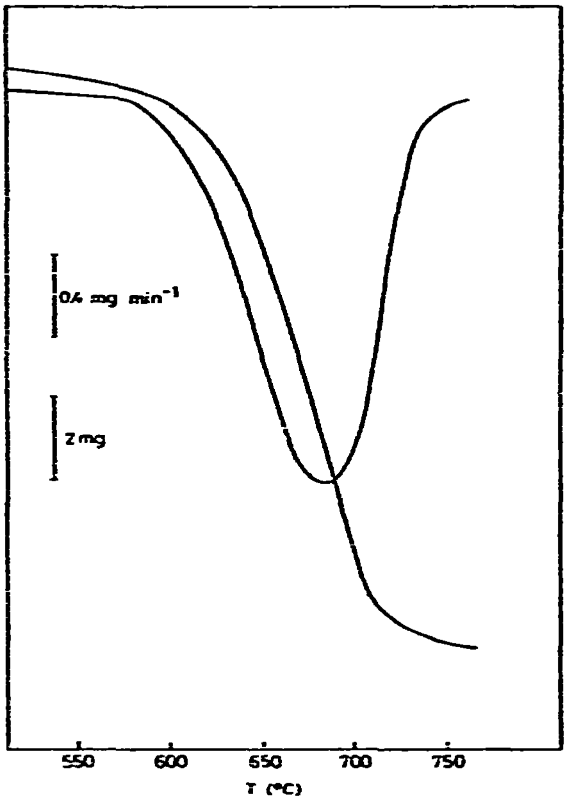

Fig. 2. TG and DTG diagrams of thermal decomposition of $CaCO_3$ obtained under a vacuum of 10^{-4} torr and a heating rate of 12°C min^{-1}.

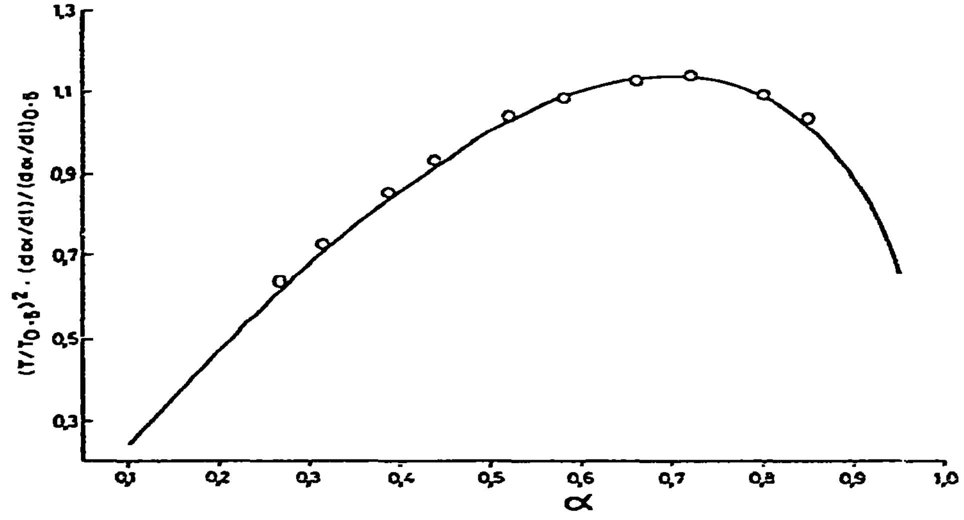

Fig. 3. Checking of the master curve corresponding to a R_3 mechanism.

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