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Note

On the estimation of the reaction mechanisms of thermal decomposition of solids from the fraction reacted at the maximum reaction rate

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A number of authors[1–3] have reported a method for determining the reaction order of thermal decomposition of solids from the value of the reacted fraction, α_m, at the maximum reaction rate. This method has been recently refined by Gyulai and Greenhow[4].

It is well established[5, 6] that n-order kinetic equations can only have theoretical meaning when the values of n are 0, 1/2, 2/3, or 1. Moreover, it is well known that solid state reactions can be described by a variety of mechanisms. The α_m values of reactions taking place via the Avrami–Erofeev mechanism were calculated in a previous publication[7] where it was reported that the values coincide with those obtained for first-order reactions.

In order to explore the real possibilities of the above-mentioned named procedure for deciding between different reaction mechanisms, this note reports our calculations of the α_m values of reactions whose rate controlling step is a diffusion process.

Reactions following a two-dimensional diffusion mechanism fit the kinetic equations:

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

and

$$(1-\alpha)\ln(1-\alpha) + \alpha = \frac{AE}{R\beta} \cdot p(E/RT) \tag{2}$$

where α is the reacted fraction, β, the heating rate, A, the preexponential Arrhenius factor; E, the activation energy, and p(E/RT) is a function given by the following expression:

$$p(E/RT) = \frac{e^{-E/RT}}{(E/RT)^2}\left[1 - \frac{2!}{E/RT} + \frac{3!}{(E/RT)^2} - \dots + \frac{(-1)^n(n+1)!}{(E/RT)^{n+1}}\right]$$

$$= \left(\frac{RT}{E}\right)^2 \cdot e^{-E/RT} \cdot g(E/RT) \tag{3}$$

Since the reaction rate reaches a maximum when $d^2\alpha/dt^2 = 0$, we can write:

$$\frac{1}{(1-\alpha_m)[\ln(1-\alpha_m)]^2} \cdot A \cdot e^{-E/RT} = \frac{E\beta}{RT^2} \tag{4}$$

From eqns. (2), (3) and (4), after rearrangement, we obtain:

$$\frac{(1-\alpha_m)\ln(1-\alpha_m) + \alpha_m}{(1-\alpha_m)[\ln(1-\alpha_m)]^2} = g(E/RT) \tag{5}$$

The values of α_m calculated from eqn. (5) and using the values of $g(E/RT)$ determined from the corresponding values of $p(E/RT)$ tabulated by Zsakó[8] are included in Table 1.

Reactions which follow the Jander diffusion mechanism fulfill the rate laws

$$\frac{d\alpha}{dt} = \frac{3}{2}\frac{(1-\alpha)^{2/3}}{[1-(1-\alpha)^{1/3}]} \cdot A \cdot e^{-E/RT} \tag{6}$$

and

$$[1-(1-\alpha)^{1/3}]^2 = \frac{ART^2}{E\beta} \cdot g(E/RT) \cdot e^{-E/RT} \tag{7}$$

By setting the first derivative of eqn. (6) equal to zero, we obtain:

$$\frac{1/2 - (1-\alpha_m)^{-1/3}}{[1-(1-\alpha_m)^{1/3}]^2} \cdot A \cdot e^{-E/RT} = \frac{E\beta}{RT^2} \tag{8}$$

which, after substituting eqns. (3) and (7), gives:

$$\alpha_m = 1 - \frac{1}{1/2 + g(E/RT)} \tag{9}$$

The values of α_m as a function of E/RT are given in Table 1.

In the case of solid state reactions which can be described by the three-dimensional diffusion mechanism of Ginstling–Brounshtein, thermogravimetric data must fit the rate laws:

$$\frac{d\alpha}{dt} = \frac{3}{2}\frac{1}{[(1-\alpha)^{-1/3} - 1]} \cdot A \cdot e^{-E/RT} \tag{10}$$

and

$$\left(1 - \frac{2\alpha}{3}\right) - (1-\alpha)^{2/3} = \frac{ART^2}{E\beta} \cdot g(E/RT) \cdot e^{-E/RT} \tag{11}$$

TABLE 1

VALUES OF α_m AS A FUNCTION OF E/RT FOR VARIOUS DIFFUSION MECHANISMS

Mechanism	*E/RT*					
	10	*20*	*30*	*40*	*50*	∞
Ginstling–Brounstein	0.680	0.729	0.745	0.752	0.758	0.776
Jander	0.587	0.644	0.665	0.673	0.680	0.704
Two-dimensional	0.752	0.795	0.808	0.814	0.819	0.833

TABLE 2

VALUES OF α_m FOR 1/2- AND 2/3-ORDER REACTIONS AS A FUNCTION OF E/RT_m

n	E/RT_m					
	10	*20*	*30*	*40*	*50*	∞
1/2	0.706	0.727	0.734	0.738	0.740	0.750
2/3	0.630	0.674	0.681	0.685	0.690	0.700

By setting $d^2\alpha/dt^2 = 0$, we get:

$$\frac{(1-\alpha_m)^{-4/3}}{2\,[(1-\alpha_m)^{-1/3}-1]^2}\cdot A\cdot e^{-E/RT} = \frac{E\beta}{RT^2} \tag{12}$$

which, solved together with eqns. (11) and (3) gives:

$$\frac{\Bigg[\Bigg(1-\frac{2\alpha_m}{3}\Bigg(-(1-\alpha_m)^{2/3}\Bigg]\cdot(1-\alpha_m)^{-4/3}}{2\,[(1-\alpha_m)^{-1/3}-1]^2} = g(E/RT) \tag{13}$$

The values of α_m as a function of E/RT are shown in Table 1.

With regard to the one-dimensional diffusion mechanism described by the kinetic equations:

$$\frac{d\alpha}{dt} = \frac{1}{2\alpha}\cdot A\cdot e^{-E/RT} \tag{14}$$

and

$$\alpha^2 = \frac{ART^2}{E\beta}\cdot g(E/RT)\cdot e^{-E/RT} \tag{15}$$

it is evident that the reaction rate continuously increases with the temperature until the reactant is exhausted. This behaviour is the same as that described[7] for zero-order reactions.

Table 2 includes the values of α_m calculated for 1/2- and 2/3-order reactions in a previous paper[3]. From Tables 1 and 2 it can be seen that the α_m values determined for 2/3-order reactions and for those reactions following the Jander diffusion mechanism are very similar. The α_m values of 1/2-order reactions and of those taking place via the Ginstling–Brounshtein mechanism are also in close agreement.

From the considerations above we can conclude that the method proposed in the literature for determining the order of thermal decomposition reaction of solids from the value of α_m would lead to a mis-interpretation of the results. In fact, is almost impossible to distinguish between reactions which follow Jander, Gistling–Brounshtein or one-diffusion mechanisms and those described by 1/2-, 2/3- or zero-order kinetic equations, respectively, as there are no important differences between the corresponding values of α_m. In a similar way, reactions proceeding via Avrami–Erofeev mechanisms would be confused with first-order reactions.

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