

FRACTAL APPROACH IN THE KINETICS OF SOLID-GAS DECOMPOSITIONS PART II

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Abstract

The author presents some applications of the fractal geometry in the kinetics of heterogeneous decomposition of solids.

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Introduction

Following our earlier research, this note deals with the fractal approach for three cases of heterogeneous solid-gas decompositions described by nucleation-growth phenomena.

Many steps nucleation with normal growth of nuclei

As shown in literature as well as in our previous note [1] for heterogeneous decompositions in solid-gas systems described by nucleation-growth, the classical theory predicts integer values for n in the integral kinetic equation [1–4]:

$$\alpha = kt^n$$

One of the reasons for the experimentally found fractionary values of n was considered the slower growth of small nuclei with respect to the larger (normal) ones [2]. Taking into account this hypothesis and combining it with the idea, according to which the nuclei exhibit a fractal character [1, 5], the total volume of the nuclei belonging to the new phase (product $B_{(s)}$) generated in the reaction



is given by the sum:

$$V(t) = \sigma_D \beta \gamma \int_0^{t-t'} [k_2'(t-y)]^D y^{\beta-1} dy - \sigma_D \beta \gamma \int_{t-t'}^t [k_2'(t-y)]^D y^{\beta-1} dy \quad (1)$$

where σ_D is the so called fractal shape factor [4], β is the number of steps necessary to form a stable nucleus, γ is a constant in the nucleation integral kinetic equation:

$$N = \gamma t^\beta \quad (2)$$

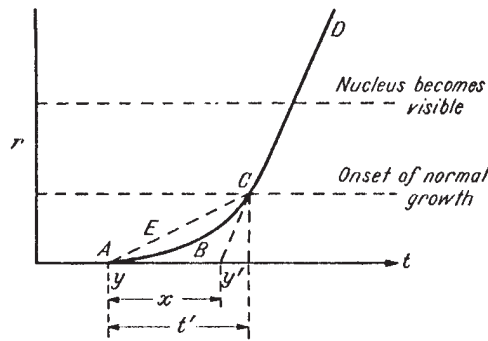


Fig. 1 Classical hypothetical time dependence of the radius of the nucleus [2]

N – being the number of the nuclei belonging to the reaction product generated at the time t and D is the fractal dimension of the nucleus $1 < D < 3$. As far as k_2 and k_2' are concerned they represent the growth rates for small and normal nuclei respectively. Other notations in relationship (1) have meanings, which result from Fig. 1 [2] and the obvious relationships:

$$\begin{aligned} r &= k_2'(t-y) \text{ for } y < t < y+t' \\ r &= k_2(t-y') \text{ for } t > y+t' \end{aligned} \quad (3)$$

where r is the radius of the nucleus. Taking into account that in the relationship

$$y' - y = t' - \frac{k_2' t}{k_2} \quad (4)$$

$k_2' > k_2$, it follows the

$$y' - y \cong t' \quad (5)$$

Under such conditions relationship (1) takes the form:

$$\begin{aligned} V(t) &= \sigma_D \beta \gamma \int_0^{t-t'} (k_2[(t-t')-y])^D y^{\beta-1} dy + \\ &+ \sigma_D \beta \gamma \int_0^t [k_2(t-y)]^D y^{\beta-1} dy - \sigma_D \beta \gamma \int_0^{t-t'} [k_2'(t-y)]^D y^{\beta-1} dy \end{aligned} \quad (6)$$

and correspondingly

$$V(t) = \sigma_D \beta \gamma k_2^D B(D+1, \beta)(t-t')^{\beta+D} + \sigma_D \beta \gamma \int_0^{t'} [k_2'(t-y)]^D y^{\beta-1} dy \tag{7}$$

where $B(p, q)$ is the function of Euler of the first kind or

$$V(t) = \sigma_D \beta \gamma k_2^D B(D+1, \beta)(t-t')^{\beta+D} + \sigma_D \beta \gamma k_2'^D \left[\frac{t^D t'^{\beta}}{\beta} - \frac{D\beta}{\beta-1} t^{D-1} t'^{\beta+1} + \frac{D(D-1)}{1.2} \frac{\beta}{\beta+2} t^{D-2} t'^{\beta+2} \pm \dots \right] \tag{8}$$

Relationship (8) is more versatile than the non-fractal one

$$\alpha = k(t-t')^n \tag{9}$$

with integers values of n . The versatility is mainly due to the non-integer values of $\beta+D=n^*$ as well as to its second term. Taking into account that $k_2' < k_2$ relationship (8) can be reduced to its first term which in terms of the conversion degree ($V(t)\alpha$) to:

$$\alpha = k^*(t-t')^{n^*} \tag{10}$$

where the exponent n^* can take fractional values too. As shown in literature [2] the integer values of n change within the range 3–8. Moreover Thomas and Tompkins determined the time t' as the time necessary to subtract from t in order to confer to the slope of the straight line $\ln p$, $\ln t$ (p being the pressure of the volatile component of the reaction I evolved at the moment t which is also directly proportional to α) exactly the value 6 [6]. Or, experience shows that n can take fractional values thus Eq. (10) as a particular form of Eq. (8) describes properly the heterogeneous decompositions in the framework of Eq. (1). This statement is confirmed by the values of n within the range 3.5–5 which have been found for the decomposition of fresh powders of silver oxalate and within the range 3.2–3.5 for the decomposition of the aged ones.

Branched nuclei which do not interact

In this case the rate of nucleation is given by the following equation:

$$\frac{dN}{dt} = k_1 N + k_3 N \tag{11}$$

where k_1 is the coefficient of one step nucleation and k_3 the branching coefficient. The integration of Eq. (11) leads to:

$$N = \frac{k_1 N_0}{k_3} (e^{k_3 t} - 1) \tag{12}$$

and correspondingly

$$\frac{dN}{dt} = k_1 N_0 e^{k_3 t} \quad (13)$$

As the nuclei are not topologically unidimensional but exhibit fractal properties it follows that the fractal length of a nucleus which began to grow at the moment y is given by

$$l_F(t, y) = k_2 (t - y)^D \quad (14)$$

where the fractal dimension is close to unity but slightly higher ($D > 1$). The total length $L_f(t)$ of the new phase generated at the moment t should then be calculated as follows.

$$L_f(t) = k_1 k_2 N_0 \int_0^t (t - y)^D e^{k_3 y} dy \quad (15)$$

Due to the fractionary value of D in order to operate the integral one has to use development in series (see appendix). Under such conditions after integration Eq. (15) turns into:

$$L(t) = k_1 k_2 N_0 e^{k_3 t} t^{D+1} \left[\frac{1}{D+1} - \frac{k_3 t}{!(D+2)} + \frac{k_3^2 t^2}{2!(D+3)} \pm \dots \right] \quad (16)$$

Taking into account that $L_f(t)$ is directly proportional to $\alpha(t)$, the kinetic equation which corresponds to the considered case is

$$\alpha(t) = \text{const.} \cdot e^{k_3 t} t^{D+1} \left[\frac{1}{D+1} - \frac{k_3 t}{!(D+2)} + \frac{k_3^2 t^2}{2!(D+3)} \pm \dots \right] \quad (17)$$

This equation is more versatile than the corresponding non-fractal one

$$\alpha = C e^{k_3 t} \quad (18)$$

which has been proved to be valid only for limited portions of the (α, t) curve (until $\alpha = 0.5$) for the decomposition of lead stiphate [9]

Random nucleation with normal growth

For the exponential nucleation law

$$\frac{dN}{dt} = k_1 N e^{-k_1 t} \quad (19)$$

and the fractal growth law

$$v(t, y) = \sigma_D k_2^D (t - y)^D \quad (20)$$

according to the general formula for the volume $V(t)$ of the product of reaction (I):

$$V(t) = \int_0^t v(t,y) \left(\frac{dN}{dt} \right)_{t=y} dy \tag{21}$$

it turns out that

$$V(t) = k_1 N_0 \sigma_D k_2^D \int_0^t e^{-k_1 y} (t-y)^D dy \tag{22}$$

Taking into account the fractional value of D and thus the impossibility to solve exactly the integral in (22), a fair good approximation is obtained using a development in series as shown in the appendix. Under such conditions Eq. (22) turns into:

$$V(t) = \sigma_D k_1 N_0 k_2^D \left(e^{-k_1 t} t^{D+1} \left[\frac{1}{D+1} + \frac{k_1 t}{1!(D+2)} + \frac{(k_1 t)^2}{2!(D+3)} + \frac{(k_1 t)^3}{3!(D+4)} + \dots \right] \right) \tag{23}$$

or as $V(t) \propto \alpha(t)$

$$\alpha(t) = \text{const.} \cdot e^{-k_1 t} t^{D+1} \left[\frac{1}{D+1} + \frac{k_1 t}{1!(D+2)} + \frac{(k_1 t)^2}{2!(D+3)} + \frac{(k_1 t)^3}{3!(D+4)} + \dots \right] \tag{24}$$

This integral kinetic law can be compared with the corresponding non-fractal one for the investigated case of heterogeneous decompositions.

$$\alpha(t) = \text{const.} \left[e^{-k_1 t} - 1 + k_1 t - \frac{(k_1 t)^2}{2!} + \frac{(k_1 t)^3}{3!} \right] \tag{25}$$

Both equations, for small values of $k_1 t$ lead to the simple kinetic equation $\alpha = \text{const.} \cdot t^n$ with fractional [4] or particularly integer values of n as in the case of ammonium chromate decomposition for which $n=4$ [10].

Conclusions

Grounded on the treatment of nuclei as fractal particles three models for the kinetics of the heterogeneous solid-gas decompositions have been presented. The models are more general and versatile than the classical non-fractal ones.

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Appendix

The integral

$$\int_0^t (t-y)^\lambda e^{k_1 y} dy \quad 1 < \lambda < 3$$

$$\int_0^t (t-y)^\lambda e^{k_i y} dy = \int_0^t (t-y)^\lambda e^{\lambda[k_i(y-0)+k_i t]} dy \quad (A_1)$$

$$\int_0^t (t-y)^\lambda e^{[r_i(y-0)+k_i t]} dy = e^{k_i t} \int_0^t (t-y)^\lambda e^{-k_i(t-y)} dy \quad (A_2)$$

$$e^{k_i t} \int_0^t (t-y)^\lambda e^{-k_i(t-y)} dy = e^{k_i t} \int_0^t (t-y)^\lambda \left[\sum_{k=0}^{\infty} (-1)^k \frac{k_i^k (t-y)^k}{k!} \right] dy \quad (A_3)$$

$$e^{k_i t} \int_0^t (t-y)^\lambda \left[\sum_{k=0}^{\infty} (-1)^k \frac{k_i^k (t-y)^k}{k!} \right] dy = e^{k_i t} t^{\lambda+1} \sum_{k=0}^{\infty} (-1)^k \frac{k_i^k t^k}{k!(\lambda+k+1)} \quad (A_4)$$

Thus

$$\int_0^t (t-g)^\lambda e^{k_i y} dy = e^{k_i t} t^{\lambda+1} \sum_{k=0}^{\infty} (-1)^k \frac{k_i^k t^k}{k!(\lambda+k+1)} \quad (A_5)$$

The integral

$$\int_0^t (t-y) e^{k_i y} dy$$

can be calculated in the same way by substituting $k_i \rightarrow -k_j$ in (A₅)

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