FRACTAL APPROACH IN THE KINETICS OF SOLID-GAS DECOMPOSITIONS

E. Segal

Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, Bulevardul Republicii 13, Bucharest, Roumania

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Abstract

The author presents a model based on multi-step nucleation for the heterogeneous decompositions described by nucleation and growth phenomena, taking into account the fractal nature of the nuclei.

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Introduction

An analysis of the heterogeneous reactions occurring in powders submitted to grinding due to Ozao and Ochiai [1] led to the following conclusions:

– the mechanical reduction of the particle sizes leads to a fractal distribution of them given by the function $P(X,t)$ where $X=x/x_e$ (x – the size of the particle scaled with a characteristic constant size, x_e) and t is the grinding time, with the form: $P(X,t)\alpha X^n$ the exponent n being a material constant,

– a particle size distribution function of a solid powder described by the mentioned power law indicates the self similarity of the particles and correspondingly their fractal character,

– the energy associated with the breakage is described by experimentally verified laws derived by considering the fractal character of the particles.

Taking into account the results of their analysis, Ozao and Ochiai [1] suggest the reconsideration of the particular forms of the differential conversion function $f(\alpha)$ in the general rate equation:

$$\frac{d\alpha}{dt} = kf(\alpha) \qquad (1)$$

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which describes heterogeneous reactions, particularly heterogeneous decompositions in solid–gas systems such as:

$$A_s \rightarrow B_s + C_g \qquad (1)$$

This note is dedicated to reactions of the form (I) whose kinetics are described by nucleation-growth mechanisms.

According to the classical theory regarding the kinetics of such reactions, the total volume of the new solid phase, B_s generated through reaction (I) at the moment t is given by the relationship [2, 3, 4]:

$$V(t) = T\int_0^t \left[\int_y^t G(x)\mathrm{d}x\right]^{\lambda} \left(\frac{\mathrm{d}N}{\mathrm{d}t}\right)_{t=y} \mathrm{d}y \qquad (2)$$

where T is a shape factor which equals 1 for the growth of nuclei in one dimension, π for the two-dimensional growth and $4\pi/3$ for the three-dimensional growth, λ equals 1, 2 or 3 for the linear, surface or volume growth, N the number of nuclei generated at the moment t, $\mathrm{d}N/\mathrm{d}t$ the rate of nucleation and $G(x)$ the growth rate. One can notice that in relationship (2) the expression

$$T\left[\int_y^t G(x)\mathrm{d}x\right]^{\lambda}$$

describes the generalized volume of a nucleus which began to grow at the moment t. It is easy to see that for various laws of nucleation and growth, relationship (2) leads to various forms of the dependence $V(t)$. As $V(t)$ is directly proportional to the degree of conversion, $\alpha(t)$, it turns out that Eq. (2) is in fact the most general integral kinetic equation which describes reactions controlled by nucleation-growth phenomena.

In the following we shall consider the multi-step temporal evolution of the number of nuclei.

$$N = \gamma t^{\beta} \qquad (3)$$

where γ is a constant and the exponent β represents the number of successive steps necessary for the formation of a stable nucleus. From relationship (3) the rate of nucleation is given by

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \beta\gamma t^{\beta-1} \qquad (4)$$

As far as the growth rate is concerned, we shall consider it as constant i.e.,

$$G(x) = k_2 = \text{const.} \tag{5}$$

Taking into account relationships (4) and (5), volume $V(t)$ according to (2) takes the form:

$$V(t) = T\int_0^t [k_2(t-y)]^\lambda \beta\gamma y^{\beta-1}\,\mathrm{d}y \tag{6}$$

Operating a binomial development followed by integration term by term one obtains:

$$V(t) = Tk_2^\lambda\gamma\left[1 - \frac{\lambda\beta}{\beta+1} + \frac{\lambda(\lambda-1)}{2!}\frac{\beta}{\beta+2} \pm \ldots\right]t^{\beta+\lambda} \tag{7}$$

Introducing the notations

$$Tk_2\gamma\left[1 - \frac{\lambda\beta}{\beta+1} + \frac{\lambda(\lambda-1)}{2!}\frac{\beta}{\beta+2} \pm \ldots\right] = C' \tag{8}$$

$$n = \beta + \lambda \tag{9}$$

relationship (7) can be retranscribed in the form:

$$V(t) = C't^n \tag{10}$$

or as $V(t) \propto \alpha(t)$ it follows that

$$\alpha(t) = Ct^n \tag{11}$$

Taking into account the meanings of β *and* λ *in relationship (9), the exponent* n should be characterized by integer values. However, among the experimentally determined values of n, fractional values have been found. Thus for the decomposition of silver oxalate the determined values of n lie in the range 3–4 [5], while for the decomposition of lead azide the determined values lie in the range 2.14–3.67 [6]. Some supplements of the nucleation-growth theory based on the idea according to which small nuclei grow more slowly than the big ones allowed to explain the fractional values of n. In our opinion another explanation could be given by taking into account the fractal character of the nuclei. Under such conditions relationship (6) and (7) turn into:

$$V(t) = T_\mathrm{D}\int_0^t [k_2(t-y)]^\mathrm{D} \beta\gamma y^{\beta-1}\,\mathrm{d}y \tag{12}$$

and

$$V(t) = T_D k_2^{\lambda}\gamma\left[1 - \frac{D\beta}{\beta+1} + \frac{D(D-1)}{2!}\frac{\beta}{\beta+2} \pm \ldots\right] t^{\beta+D} \qquad (13)$$

where D is the fractal dimension of the nucleus ($1<D<3$) and T_D is the 'fractal' shape factor which obviously differs from T. Taking again into account the proportionality between $V(t)$ and $\alpha(t)$ and introducing the notations:

$$T_D k_2^{D}\gamma\left[1 - \frac{D\beta}{\beta+1} + \frac{D(D-1)}{2!}\frac{\beta}{\beta+2} \pm \ldots\right] = C^* \qquad (14)$$

$$\beta + D = n^* \qquad (15)$$

relationship (13) turns into:

$$\alpha(t) = C^* t^{n^*} \qquad (16)$$

an integral kinetic equation which can be compared with (11) but in which, taking into account the meaning of the fractal dimension D and according to (15), the exponent n^* should be fractional.

A more general way of integration either in (6) or in (12) is based on the change of variables:

$$y = tz \qquad (17)$$

Under such conditions relationship (6) and (12) turn respectively into

$$V(t) = \gamma\beta T k_2^{\lambda} B(\lambda+1, \beta) t^{\beta+\lambda} \qquad (18)$$

and

$$V(t) = \gamma\beta T_D k_2^{D} B(D+1, \beta) t^{\beta+D} \qquad (19)$$

where $B(p, g)$ is the Euler integral of the first kind. It is easy to notice the equivalence of relationships (18) and (19) with relationships (7) and (13) from the standpoint of the dependences $V(t)$ and correspondingly $\alpha(t)$.

Relationships (18) and (19) are more general than a similar relationship derived by Ozao and Ochiai [1] which considered only the case characterized by $\beta=1$ which corresponds to monostep nucleation.

From relationship (16) through rearrangement and differentiation one obtains successively:

$$t \propto \alpha^{\frac{1}{D+\beta}} \tag{20}$$

$$dt \propto \alpha^{\frac{1-D-\beta}{D+\beta}} d\alpha \tag{21}$$

$$\frac{d\alpha}{dt} \propto \alpha^{\frac{D+\beta-1}{D+\beta}} \tag{22}$$

a rate equation which for β=1 takes the particular form derived by Ozao and Ochiai [1].

For the case of interactions between nuclei which overlap during their growth as shown by Avrami [6],

$$d\alpha' = \frac{d\alpha}{1-\alpha} \tag{23}$$

where α' is the degree of conversion in the absence of interactions. From (23) through integration one obtains

$$\alpha' = -\ln(1-\alpha) \tag{24}$$

a relationship which leads to:

$$\frac{d\alpha}{dt} = (1-\alpha)\frac{d\alpha'}{dt} \tag{25}$$

Considering that $d\alpha'/dt$ on the right hand side of Eq. (25) is given by an equation of the form (22) and taking into account (24), the following rate equation can be obtained:

$$\frac{d\alpha}{dt} = (1-\alpha)[-\ln(1-\alpha)]^{\frac{D+\beta-1}{D+\beta}} \tag{26}$$

a result which, for β=1, takes the particular form derived by Ozao and Ochiai [1].

Conclusions

General kinetic equations for heterogeneous solid–gas decomposition described by nucleation–growth mechanisms have been derived considering the fractal nature of the nuclei and a multistep nucleation rate. The derived equations have the particular forms derived by Ozao and Ochiai for monostep nucleation and lead to results in qualitative agreement with experimental data.

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