Thermochimica Acta, 220 (1993) 191–201
Elsevier Science Publishers B.V., Amsterdam

Thermal analysis and self-similarity law in particle size distribution of powder samples.
Part 4

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(Received 17 August 1992; accepted 31 August 1992)

Abstract

Well known functions for describing reaction models are reconsidered by taking the fractal nature of powder into account. The functions need not be confined only to those derived by assuming reactions on regularly shaped models such as disks, cylinders, etc. Three types of reaction model function, based on a more physically meaningful picture, are provided.

INTRODUCTION

Reaction mechanisms, at least in the field of thermal analysis, seem to be well established, and various types of functions describing such mechanisms have been proposed (see, for example, Sharp et al. [1]). Our previous reports on the fractal nature of powder inclusive of an energy law for size reduction [2] and thermal decomposition [3–5] suggest that the reaction rate of a solid subjected to a mechanical size reduction is a function of the surface fractal dimension D which relates the specific surface area of a powder S, to the statistical fractal particle size x by the power scaling law $S \propto x^{D-3}$ [4, 6]. The power D then becomes a material-dependent value, provided that the powder system under consideration is obtained by grinding for a sufficiently long time. Such a powder can be described by a characteristic particle size $x_e(t)$, which is a function of grinding hours t, and an undersieve particle size distribution function $P(X, t)$. This particle size distribution also obeys a power law $P(X, t) \propto X^{\beta}$, where X is the particle size x scaled with $x_e(t)$. We have concluded until now that the input energy for the size reduction of a solid is used mainly for the formation of a fractal

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surface with fractal dimension D [7], and that in the case of thermal decomposition, the rate thereof is also a function of D [6].

This function for the reaction rate, which we here denote by $\mathrm{d}\alpha/\mathrm{d}t$ (where α is the degree of conversion) was found, at least in thermal analysis, not to obey the simple relation $\mathrm{d}\alpha/\mathrm{d}t \propto X^{D-3} \propto S$ [6]. In other words, the reaction rate is not similar to that of a homogeneous reaction. The fact that the decomposition rate does not change significantly with 30% increase in surface area excludes the application of a theory valid for a homogeneous reaction to the reaction under consideration.

Avnir and co-workers (see, for example, the summary in ref. 8, and references cited therein) have carried out numerous fractal analyses in an attempt to characterize a property of an object with a scale (or a yardstick) using a power-law scaling relation property $\propto$ scale^D. Although many properties such as physisorption monolayer, chemisorption capacity, and adsorbate surface reaction rate were found to obey the power law function above, with the particle size being the scale, the reaction rates at the solid interface could not be related to the surface roughness fractal dimension by a simple power law.

Thus, how is the reaction rate related to the particle size x, if the relation

$$\text{reaction rate in a heterogeneous system} \propto x^D$$

is not valid? As a step in considering this problem, we review the known rate functions conventionally used in the field of thermal analysis. The functions have been taken from the widely used classification by Sharp et al. [1].

REACTION IN HETEROGENEOUS SYSTEMS

We describe a heterogeneous reaction in terms of a degree of conversion α as

$$\alpha = V/V_0 \tag{1}$$

where the volume V of the reacted portion is selected as the changing property to be monitored during the reaction, and V_0 is the initial volume of the system. Then, the reaction rate can be expressed as

$$\mathrm{d}\alpha/\mathrm{d}t = (1/V_0)\,\mathrm{d}V/\mathrm{d}t \tag{2}$$

If we assume that the rate is described as in the homogeneous reaction

$$\mathrm{d}\alpha/\mathrm{d}t = k(T)F(\alpha) \tag{3}$$

where

$$k(T) = Z\exp(-E/RT) \tag{4}$$

TABLE 1

Commonly used reaction function forms[a]

Symbol	Function form $F(\alpha)$	Ref.
D_1	α^{-1}	
D_2	$[-\ln(1-\alpha)]^{-1}$	1
D_3	$(1-\alpha)^{1/3}[(1-\alpha)^{-1/3}-1]^{-1}$	10
D_4	$[(1-\alpha)^{-1/3}-1]^{-1}$	11
R_2	$(1-\alpha)^{1/2}$	12
R_3	$(1-\alpha)^{2/3}$	12
F_1	$1-\alpha$	
A_2	$(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	13, 14
A_3	$(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	13, 14

[a] In accordance with the classification of Sharp et al. [1].

with Z the pre-exponential factor, E the activation energy, R the gas constant, and T the absolute temperature, and that the reaction occurs in a very narrow temperature range, we obtain

$$d\alpha/dt \propto F(\alpha) \tag{5}$$

where the function $F(\alpha)$ depends on the physical and geometric relations at the boundary between the product and the initial material. Various types of $F(\alpha)$ have been proposed, mostly independently, by many authors. In Table 1 the most basic and commonly used ones are listed, in accordance with the classification by Sharp et al. [1].

Here we assume three simple processes: (1) a surface-controlled reaction in which the chemical reaction is the rate-controlling process; (2) a diffusion-controlled reaction in which the mass transport of a material is the rate-controlling process; (3) a nucleation-dependent process in which the rate of nucleation formation and overlap of the formed and growing nuclei is rate-controlling.

Surface-controlled reaction

We assume that the reaction rate is proportional to the surface area A of the reacting boundary

$$dV/dt = kA \tag{6}$$

where k is a constant; with eqn. (2) we obtain

$$d\alpha/dt = k/V_0A \tag{7}$$

If we assume that the morphology of the reacting particle is essentially the same during the reaction, the initial volume V_0 and the unreacted or remaining volume V' can be written as

$$V_0 = Cr_0^D$$
$$V' = Cr'^D$$

where r' is the fractal size of the unreacted particle. Then, by adopting Mandelbrot's theory of co-dimension [9], the area A of the reaction boundary can be expressed by $A = C'r^{D-1}$. By simple substitution using $V = V_0 - V'$ and eqn. (1), we can rewrite eqn. (7) as

$$\mathrm{d}\alpha/\mathrm{d}t \propto (1-\alpha)^{(D-1)/D}$$

with D a fractal dimension of $2 \leqslant D \leqslant 3$.

Diffusion-controlled reaction

The rate of diffusion of a substance in a thin boundary layer between the initial material and the reacted product corresponds to the reaction rate. Here, the reacting volume is assumed to be proportional to the diffused amount, expressed by

$$\mathrm{d}V/\mathrm{d}t = K\,\mathrm{d}N/\mathrm{d}t \tag{8}$$

where N is the quantity of the diffusing material and K is a constant.

By assuming a simple one-dimensional diffusion, we obtain $\mathrm{d}^2N/\mathrm{d}r^2 = 0$ according to Fick's second law; by further assuming the concentration gradient along the direction of the diffusion to be constant, we obtain $\mathrm{d}N/\mathrm{d}r$ = constant and

$$\mathrm{d}V/\mathrm{d}t = K\,\mathrm{d}N/\mathrm{d}t = -D'KA\,\mathrm{d}N/\mathrm{d}r \tag{9}$$

where D' is the diffusion constant and A is the cross sectional area of the reaction system.

At any position r from an arbitrary origin in the product layer of a D-dimension particle, the diffusion flux per unit time becomes constant irrespective of r. Thus, by integration, eqn. (9) becomes

$$\frac{\mathrm{d}N}{\mathrm{d}t}\int_{r_0}^{r} -r^{-(D-1)}\,dr \propto \int_{N_0}^{N}\mathrm{d}N \tag{10}$$

where $1 \leqslant D \leqslant 3$.

Thus, from eqn. (10) and $\Delta N = N - N_0 > 0$, when $1 \leqslant D < 2$ we obtain

$$\mathrm{d}N/\mathrm{d}t \propto \Delta N[-r^{(2-D)} + r_0^{(2-D)}]^{-1} \tag{11}$$

when $D = 2$ we obtain

$$\mathrm{d}N/\mathrm{d}t \propto \Delta N[-\ln(r/r_0)]^{-1} \tag{12}$$

and when $2 < D \leqslant 3$ we obtain

$$dN/dt \propto \Delta N[r^{(2-D)} - r_0^{(2-D)}]^{-1} \quad (13)$$

By substituting $r/r_0 = (1 - \alpha)^{1/D}$, we obtain

$D_D\ (1 \leqslant D < 2)$ $\quad d\alpha/dt \propto [-(1 - \alpha)^{(2-D)/D} + 1]^{-1}$

$D_D\ (2 < D \leqslant 3)$ $\quad d\alpha/dt \propto [(1 - \alpha)^{(2-D)/D} - 1]^{-1}$

$D_D\ (D = 2)$ $\quad d\alpha/dt \propto [-\ln(1 - \alpha)]^{-1}$

Nucleation-dependent process

The rate in this process is assumed to be controlled by the nucleation-growth mechanism, following the basic concept established by Avrami [13] and Erofeyev [14]. Here it is assumed that the rate of forming the germ nuclei and the rate of growth thereof are each constant. Hence

$$dN/dt = kN_0 \quad (14)$$

$$v = K(k't)^D \quad (15)$$

where N is the number of nuclei, v is the volume of a nucleus, D is the fractal dimension of the direction of growth, and k and k' are rate constants for the formation of nuclei and for the growth of grains, respectively. N_0 is the number of sites suitable for nucleus formation and K is a volume conversion factor.

The total volume V for the nuclei having formed in the initial stage can be obtained from eqns. (14) and (15) as

$$V = Kk'^D \int_0^t (t - \tau)^D (dN/dt)\, d\tau$$

$$= 1/(D + 1) K N_0 k k'^D t^{D+1} \quad (16)$$

By differentiation and substitution, we obtain from eqn. (16)

$$d\alpha/dt \propto \alpha^{D/(D+1)} \quad (17)$$

If the nucleation completes in the initial stage, the total volume V after time t becomes

$$V = KNk'^D t^D$$

thus

$$d\alpha/dt \propto \alpha^{(D-1)/D} \quad (18)$$

If the grains grow large enough to impinge upon one another, the actual amount reached α is related to the theoretical α' by

$$\alpha' = -\ln(1 - \alpha)$$

TABLE 2

Functional forms with non-integer values of D

Symbol	Functional form $F(\alpha)$
$D_D(D=1\text{-}2; D\neq 2)$	$[-(1-\alpha)^{(-D+2)/D}+1]^{-1}$
$D_D(D=2\text{-}3; D\neq 2)$	$[(1-\alpha)^{(-D+2)/D}-1]^{-1}$
D_2	$[-\ln(1-\alpha)]^{-1}$
$R_D(D=2\text{-}3)$	$(1-\alpha)^{(D-1)/D}$
$A_D(D=1\text{-}3)$	$(1-\alpha)[-\ln(1-\alpha)]^{(D-1)/D}$

Thus we obtain

$$d\alpha/dt = (1-\alpha)\, d\alpha'/dt \tag{19}$$

If the nucleation proceeds at a constant rate, from eqns. (17) and (19) we obtain

$$d\alpha/dt \propto (1-\alpha)[-\ln(1-\alpha)]^{D/(D+1)}$$

If nucleation completes at the initial stage of reaction, from eqns. (18) and

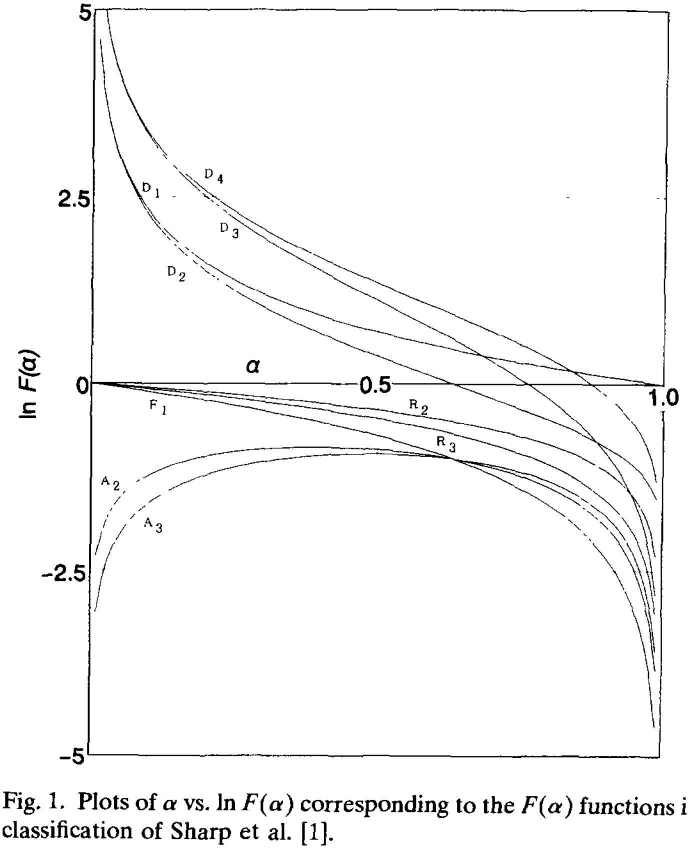

Fig. 1. Plots of α vs. $\ln F(\alpha)$ corresponding to the $F(\alpha)$ functions in Table 1 according to the classification of Sharp et al. [1].

(19) we obtain

$$d\alpha/dt \propto (1-\alpha)[-\ln(1-\alpha)]^{(D-1)/D}$$

where $1 \leqslant D \leqslant 3$.

Then we can summarize reaction functions with non-integer values of D as in Table 2. By simple substitution of D with 1, 2, or 3, the functional forms corresponding to those in Table 1 can be readily reproduced, except for $A_1 = F_1$ (in Table 1) and $D_3 = D_4$ (in Table 1), because D_3 in Table 1 is the Janderian equation, which holds only when many simplifying assumptions are satisfied.

DISCUSSION

Figure 1 shows that α vs ln $F(\alpha)$ plots corresponding to the known $F(\alpha)$ functions in Table 1. The generalized reaction functions with non-integer D listed in Table 2 are shown in Figs. 2–4.

Figure 2 shows the α vs. ln $F(\alpha)$ plot curves for the surface-controlled

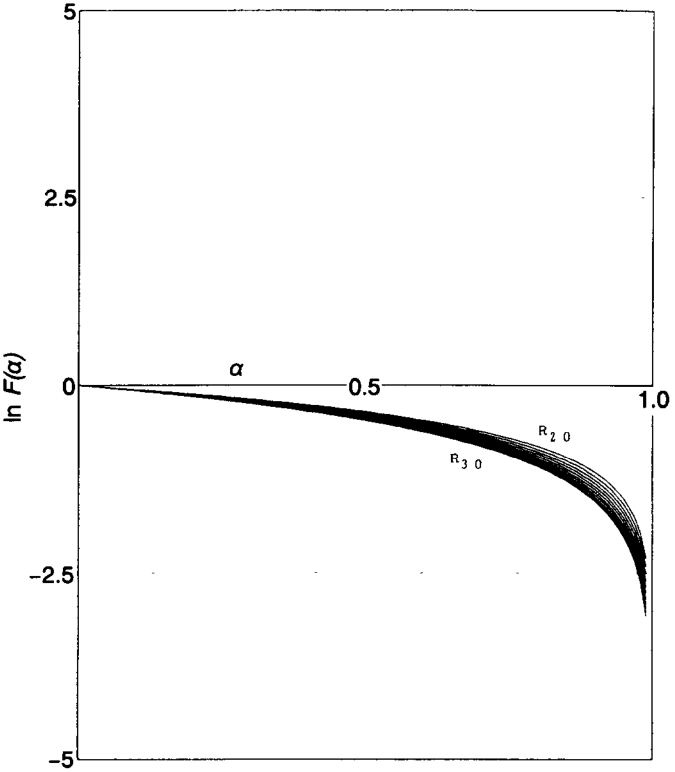

Fig. 2. Plots of α vs. ln $F(\alpha)$ for the surface-controlled reactions, indicated with symbol R_D, where D is increased from 2 to 3 in steps of 0.1. Note that the α vs. ln $F(\alpha)$ plots fall within the area defined between the conventional R_2 and R_3 curves.

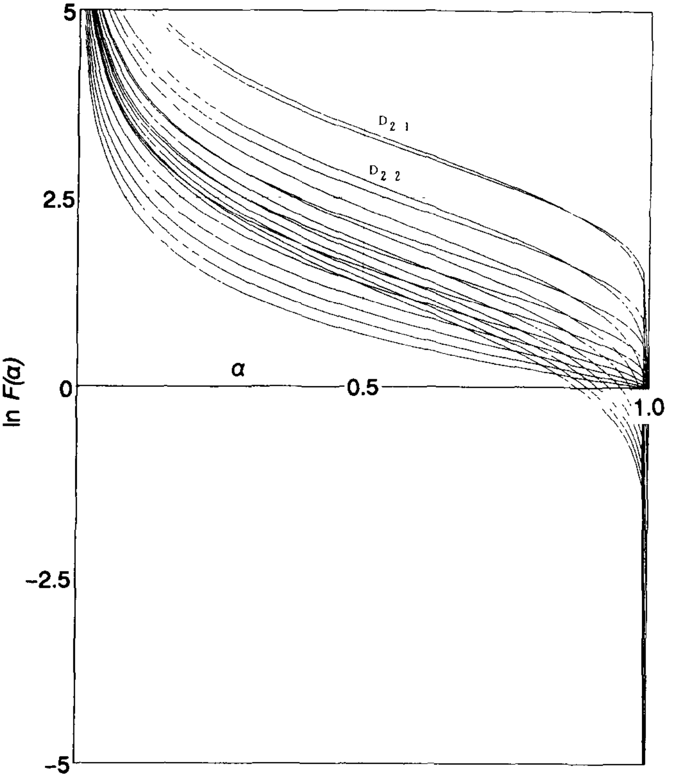

Fig. 3. Plots of α vs. $\ln F(\alpha)$ for diffusion-controlled reactions indicated by D_D, with $D = 1.0$–1.9 and $D = 2.1$–3.0 in steps of 0.1. The curve with $D = 2$ coincides with the D_2 curve in Fig. 1. Note that the curves shift to the upper side of the graph with increasing values of D to 1.9, and then shift downward from $D = 2.1$–3.0 to cover an area defined between the conventional D_2 and D_4 curves.

reactions, i.e. those indicated with symbol R_D, where D is increased from 2 to 3 in steps of 0.1. Thus, if a sample undergoes a reaction with its α vs. $\ln F(\alpha)$ plot falling within the area defined between the R_2 and R_3 curves, the reaction mechanism for such a sample may obey a surface-controlled reaction.

Figure 3 gives the α vs. $\ln F(\alpha)$ plots for diffusion-controlled reactions D_D. Very distinguished features obtained as a result of introducing a fractal concept in the reaction of solids can be observed. Those plots were made from $D = 1.0$ to 1.9, and from $D = 2.1$ to 3.0 with an interval of 0.1. The curve with $D = 2$ coincides with the D_2 curve in Fig. 1. It can be seen that the curves shift to the upper side of the graph with increasing values of D to 1.9. These curves with values of D from 1.0 to 1.9 have never been discussed as being proper for describing reaction mechanisms before adopting the concept of a non-integer dimension. The D_D curves with $D = 2.1$–3.0 cover an area defined between the conventional D_2 and D_4 curves.

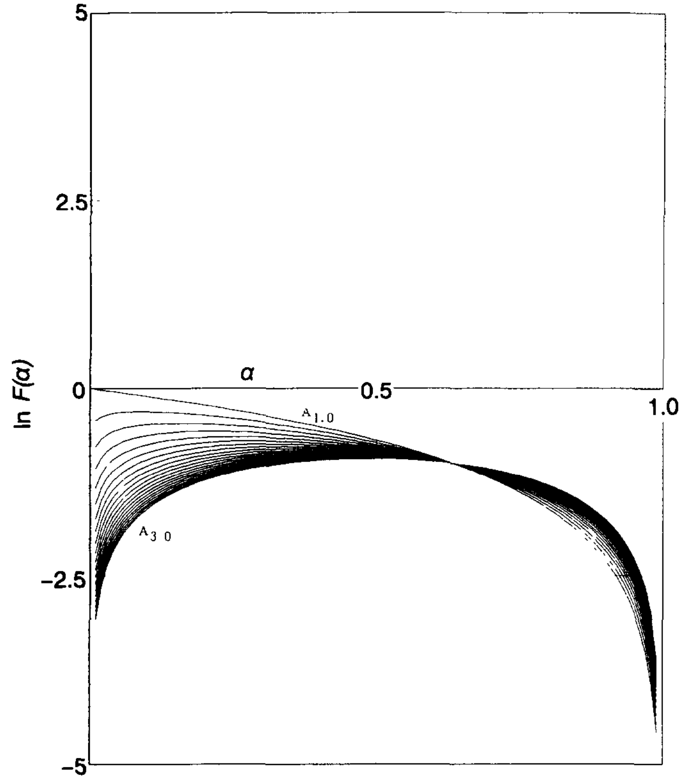

Fig. 4. Plots of α vs. $\ln F(\alpha)$ for $F(\alpha)$ functions corresponding to A_D. The curves fall between A_1 and A_3 curves in Table 1, except that A_1 corresponds to the F_1 curve in the conventional description.

Figure 4 shows the α vs. $\ln F(\alpha)$ curves for $F(\alpha)$ functions corresponding to A_D. The same discussion holds for those curves as for the D_D and R_D curves above, except that A_1 corresponds to the conventional F_1 curve.

We have shown in Parts 1 to 3 [3, 5, 6] of the present series of papers that a mechanical size reduction of a bulk into a powder yields a powder product having not only a fractal particle size distribution, but also fractal surfaces. To show the close relationship between the size reduction process and the formation of fractal surface, we provide a generalized fractal energy law for the size reduction of a solid bulk by assuming that the input energy for crushing, grinding, etc., is consumed for newly producing fractal surfaces [7]. That is, the well-known energy laws for size reduction of solid bulk such as Rittinger's law

$$E = C_R\left(\frac{1}{x_2} - \frac{1}{x_1}\right)$$

where E is the energy consumed for breakage of a particle having a size x_1 into a product with a size x_2, qwhich is the same for the laws hereinafter, and C_R is a constant; Bond's law

$$E = C_B\left(\frac{1}{\sqrt{x_2}} - \frac{1}{\sqrt{x_1}}\right)$$

where C_B is a constant; and Kick's law

$$E = C_K \log \frac{x_1}{x_2}$$

where C_K is a constant; can be all obtained by assuming that the power input is expressed by

$$dE \propto x^{D-4}\, dx$$

where D is the fractal dimension, and by putting $D = 2$, 2.5 and 3, respectively.

We have also shown [3, 5, 6] that the reactions of powder products as observed by thermal analysis are greatly influenced by the fractal particle size distribution and thereby the fractal surface, but not in a simple manner such that the reaction rate is related to the surface area by a power law.

The conventional kinetic model functions were derived on physical-geometrical assumptions based on a Euclidean geometry. However, discrepancies are often encountered between those functions and the observed reactions. Accordingly, empirical functions are recognized to be more useful for the description of a real process [15]. Our approach is different from those. We start from conventional functions but assume that a reaction proceeds on a fractal surface or in a fractal topology. The three types of model here are still too simple for the real reactions and for those involving catalytic reactions, parallel reactions, reversible reactions, etc.; however, they may describe the reactions better than those functions based on one-, two-, and three-dimensions.

CONCLUSIONS

Based on Parts 1 to 3 [3, 5, 6] of the present series of our reports, we conclude that a reaction process of a mechanically ground product is greatly affected by the fractal particle size distribution and surface. As support for this conclusion, we also show that the empirically or experimentally obtained energy laws for grinding processes describe the formation of fractal surfaces. We propose here three types of function for describing a heterogeneous reaction process instead of the conventional functions.

Because inorganic samples are used in powder form in thermal analysis, it is more natural to assume reactions involving a non-integer dimension because it is well established at present that a powder obtained by a mechanical size-reduction process is composed of particles having a surface defined by fractal dimension.

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