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KINETIC EQUATIONS FOR THERMAL DISSOCIATION PROCESSES
Part II. Equations R2 and F0

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Abstract

Relationships have been established between the average conversion degree and the dissociation time for polydisperse granular material, taking into account its grain size distribution. It has been checked in which cases the kinetic curves, obtained by a numerical solution, can be described in terms of equations R2 and F0.

Keywords: kinetics in polydisperse systems, thermal dissociation of solids

Introduction

The first part of our paper was devoted to a description of the macromechanism of thermal dissociation of solids in terms of known kinetic equations based on a single grain model [1–10]. In a case of a polydisperse system (with differentiated grain size) the degree of conversion is different for grains of different initial dimensions (R_i). It can be described by the following relation:

$$\overline{\alpha}=1-\int_{R_i=0}^{R=R_m}[1-\alpha(R_i)]f(R)\mathrm{d}R \tag{1}$$

where $\overline{\alpha}$ – mean value of transformation degree, $\alpha(R_i)\in<0;1>$, $\alpha(R_i)$ – transformation degree for grainfraction of initial radius R_i, $f(R)$ – density function for grain size distribution, characteristic for the given polydisperse system, R_m – final radius of the coarsest grains present in the reaction system.

The aim of the present part of the paper was to check the possibility of using other kinetic equations for the description of thermal dissociation processes occurring in polydispersed systems. As the first for testing we have chosen the following equation R2:

$$1-(1-\alpha)^{1/2}=kt \tag{2}$$

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often referred to as equation of 'surface contraction' or equation of 'contracting disc'. Equation (2) has been utilised for description of many thermal dissociation reactions. It has been derived with assumptions that the process of thermal dissociation of the type $A_{(st)}+B_{(st)}+C_{(g)}$ proceeds by instantaneous formation of nuclei of the new phase (reaction product) on the surface of the reacting cylindrical or prism-shaped grain, or the nuclei of the new phase are not formed on some crystal faces and the migration of the phase boundary substrate-product (reaction boundary) is considered only for those crystal planes on which the nuclei have been formed.

The exponent reflexes the number of directions in which the phase boundary propagates; Eq. (2) described volume contraction if it is 1/3 and surface contraction if the value is 1/2. If the exponent value is 1 the equation describes the cases where the phase boundary migrates with a constant rate in one direction. It means that Eq. (2) becomes Eq. (3) which is equation of zero order F0:

$$\alpha = kt \tag{3}$$

This equation describes very well the cases where the reaction surface is constant and it does not shift inside the grain bulk. Such cases occur e.g. during the desorption of mobile water molecules from that surface and in cases where the substrate molecules are not planar and where the crystallographic factors do not favour a single direction of migration of the phase boundary. We have checked the possibility of using the equations R2 and F0 for mathematical description of thermal dissociation of polydisperse solids for such systems in which the grain size distribution is described in terms of either normal or Rosin–Ramler–Sperling distribution i.e. where the functions of density of the grain size distribution are given, respectively, by the following equations:

$$f_N(R) = \frac{1}{\delta\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{R-\bar{R}}{\delta}\right)^2\right] \tag{4}$$

$$\varphi_{\Re}(R) = n\left(\frac{1}{R}\right)^n R^{n-1} \exp\left[-\left(\frac{R}{\bar{R}}\right)^n\right] \tag{5}$$

and the distribuants are expressed by the following relationships:

$$F_N(R) = \sqrt{\frac{B}{\pi}} \int_{-\infty}^{R_z} \exp[-B(R_z-1)^2]\mathrm{d}R_z \tag{6}$$

$$\Phi_{\Re}(R) = 1-\exp(-R_z^n) \tag{7}$$

In the above equations: δ – variance, $\bar{R}$ – mean grain radius, $B=\frac{\bar{R}}{2\delta^2}$, $R_z=\frac{R}{\bar{R}}$.

Formulation of the problem

The dimensionless variable $R_z=R/\overline{R}$ is inserted into Eqs (2) and (3) and maximum time of transformation is calculated for a fraction of radius R_i. From Eqs (2) and (3) it follows that the maximum time of transformation of *i*-th fraction for $\alpha=1$ is $t_{m,i}$.

Assuming in Eq. (2) $k=k_i/R_i$ one obtains for a fraction of R_i and $\alpha=1$:

$$t_{m,i}=\frac{R_i}{k_i}=\frac{R_{z,i}\overline{R}}{k_i} \tag{8}$$

hence:

$$\theta_{k,i}=\frac{k_{1,i}t_{m,i}}{\overline{R}}=R_{z,i} \tag{9}$$

An analogous procedure is applied for Eq. (3).

The transformed Eq. (2) and the density function $f_N(R)$ are inserted into Eq. (1) and assumption is made that $dR=\overline{R}\,dR_z=\overline{R}\,d\theta$, hence:

$$\overline{\alpha}=1-\left\{\int_{R=0}^{R=R_m}\left[1-\alpha(R_i)]\frac{1}{\delta\sqrt{2\pi}}\exp\left[-\frac{1}{2}\left(\frac{R-\overline{R}}{\delta}\right)^2\right]dR\right.\right\} \tag{10}$$

Assuming $\overline{R}=1$ we obtain $\theta_{k,i}=k_it_{m,i}$ hence:

$$\alpha(R_i)=1-(1-\theta)^2 \tag{11}$$

An analogous procedure on Eq. (3) gives:

$$\alpha(R_i)=\theta \tag{12}$$

and Eq. (2) assumes the form:

$$\overline{\alpha}=1-\left\{\int_{\theta_1}^{\theta_m}\left[(1-\theta)^2\frac{1}{\delta\sqrt{2\pi}}\exp\left[-\frac{1}{2}\left(\frac{R-1}{\delta}\right)^2\right]\right]d\theta\right\} \tag{13}$$

and Eq. (3) becomes:

$$\overline{\alpha}=1-\left\{\int_{\theta_1}^{\theta_m}\left[(1-\theta)\frac{1}{\delta\sqrt{2\pi}}\exp\left[-\frac{1}{2}\left(\frac{R-1}{\delta}\right)^2\right]\right]d\theta\right\} \tag{14}$$

Equations (13) and (14) comprise the terms $1/\delta\sqrt{2\pi}$ and $-1/2[(R-1)/\delta]^2$. We can introduce a dimensionless variable $B=1/2\delta^2$ in the former and assume $\overline{R}=1$.

Hence we obtain:

$$\delta=\sqrt{\frac{1}{2B}} \tag{15}$$

For δ^2 the latter equation assumes the form:

$$-\frac{1}{2}\frac{(R-1)^2}{\delta^2}=-\frac{1}{2}\left(\frac{(R-1)^2}{\frac{1}{2B}}\right)=-B(\theta-1)^2 \tag{16}$$

After introduction of relationships (15) and (16) to Eqs (13) and (14), respectively, and for $\mathrm{d}R=\bar{R}\mathrm{d}R_z=\bar{R}\theta$ one obtains in the case of Eq. (2) for the normal distribution and Rosin–Rammler–Sperling distributions, respectively:

$$\bar{\alpha}=1-\left\{\frac{\sqrt{B}}{\pi}\int_{\theta_1}^{\theta}(1-\theta_1)^2\exp[-B(\theta-1)^2]\mathrm{d}\theta\right\} \tag{17}$$

$$\bar{\alpha}=1-\left\{n\int_{\theta_1}^{\theta}(1-\theta_1)^2\theta^{n-1}\exp[-\theta^n]\mathrm{d}\theta\right\} \tag{18}$$

and for Eq. (3):

$$\bar{\alpha}=1-\left\{\frac{\sqrt{B}}{\pi}\int_{\theta_1}^{\theta_m}(1-\theta_1)\exp[-B(\theta-1)^2]\mathrm{d}\theta\right\} \tag{19}$$

$$\bar{\alpha}=1-\left\{n\int_{\theta_1}^{\theta_m}(1-\theta_1)\theta^{n-1}\exp[-\theta^n]\mathrm{d}\theta\right\} \tag{20}$$

Calculations, results and discussion

Equations (17), (18), (19) and (20) have no analytical solutions.

The following method has been applied for performing numerical calculations in the language Turbo Pascal 6.0:

The calculations were performed for the values of B and θ in the case of normal distribution and for n and θ in the case of Rosin–Rammler–Sperling distribution.

The values of $\bar{\alpha}$ for $B\in<0.001;1000>$ and for $\theta\in<0.001;2>$ were calculated from Eqs (17) and (19) . After necessary search among B values we have those for which the kinetic curves begin at the origin as in Figs 1a and 1b.

The kinetic curves determined have been described in terms of Eqs (2) and (3). The results of calculations are given in Figs 3a and 3b.

In the same way the values of $\bar{\alpha}$ for $n\in<0.001;1>$ and $\theta\in<0.001;2>$ were calculated from Eqs (18) and (20) (Figs 5a and 5b).

The kinetic curves found were described in terms of Eqs (2) and (3). The results of calculations are given in Figs 6a and 6b.

The kinetic curves for normal distribution starting at the origin and obtained for selected values of B=5; 6; 7; 8; 9; 10 in terms of Eq. (2) and for values of B=4; 5; 6; 7;

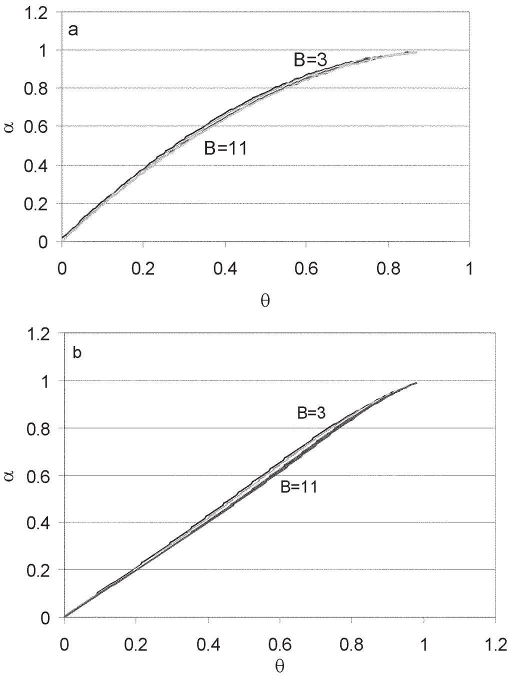

Fig. 1 Kinetic curves: values for $B\in<3;11>$: a – for Eq. R2, b – for Eq. F0

8; 9 by Eq. (3) are shown in Figs 2a, 2b, 4a and 4b. Analogous curves for the case of Rosin–Rammler–Sperling distribution were obtained for Eq. (2) if $n\in<0.041:0.05>$, and for Eq. (3) if $n\in<0.04:0.05>$. The obtained results are shown in Figs 7a and 7b.

The description of a kinetics in terms of Eq. (2) with a condition:

$$B=\frac{\overline{R}^2}{2\delta^2}\geq 5 \tag{21}$$

means that for $\overline{R}=1$ the mean deviation cannot exceed 0.316 ($\delta\leq 0.316$), and a description by means of Eq. (3) with a condition:

$$B=\frac{\overline{R}^2}{2\delta^2}\geq 4 \tag{22}$$

means that for $\overline{R}=1$ the mean deviation cannot exceed 0.3535 ($\delta\leq 0.3535$).

Hence a mathematical description of the processes under consideration in terms of Eqs (2) and (3) becomes possible if the value of R remains within the limits $0.5R\leq R\leq 1.5R$ i.e. if the variability range of R is relatively small.

In the case of polydisperse solid material with Rosin–Rammler–Sperling distribution the nature of the distribution depends on the value of n, and the distribuants

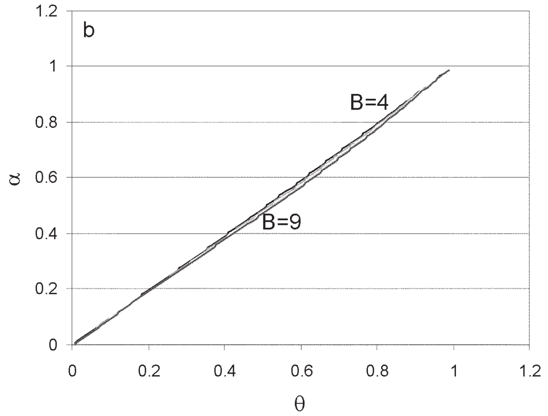

Fig. 2 Kinetic curves for selected values of *B*∈<5;10>: a – in Eq. R2 and *B*∈<4;9>: b – in Eq. F0

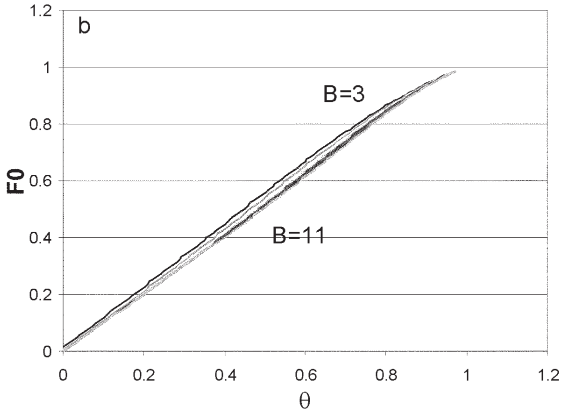

Fig. 3 Kinetic curves for the values of *B*∈<3;11>, calculated from : a – Eq. R2, b – Eq. F0

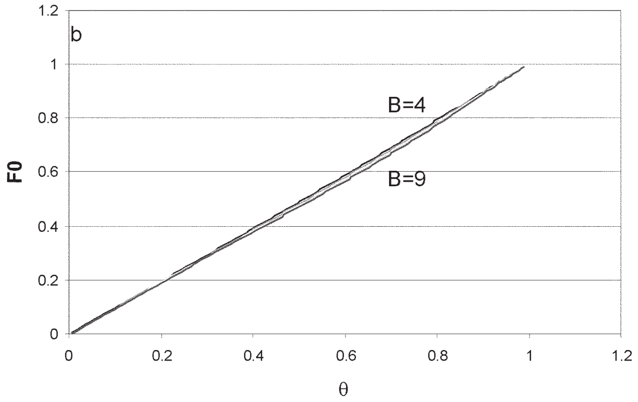

Fig. 4 Kinetic curves calculated for Eqs R2 and F0: a – for *B*∈<5;10>, b – for *B*∈<4;9>

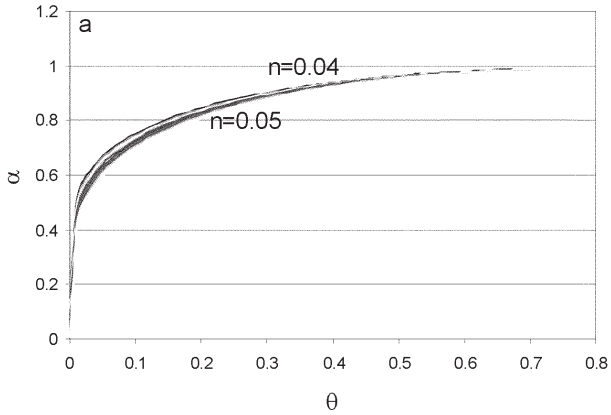

Fig. 5 Kinetic curves for the values of $n\in$<0.04;0.05>: a – for Eq. R2, b – for Eq. F0

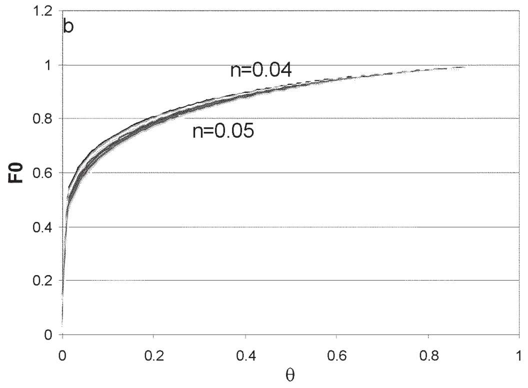

Fig. 6 Kinetic curves for the values of $n\in$<0.041;0.05> and $n\in$<0.041;0.05>for the equations: a – R2, b – F0

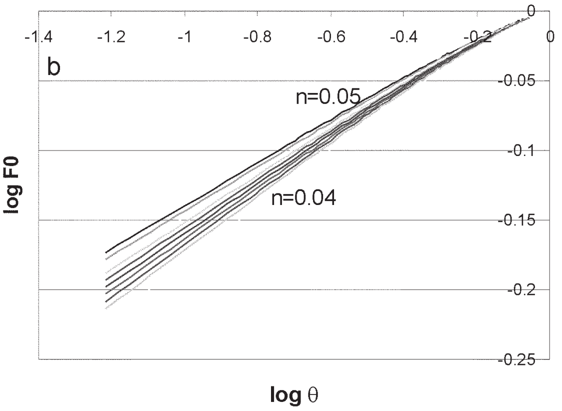

Fig. 7 Logarithms of Eqs R2 and F0: a – for $n\in$<0.041;0.05>, b – for $n\in$<0.04;0.05>

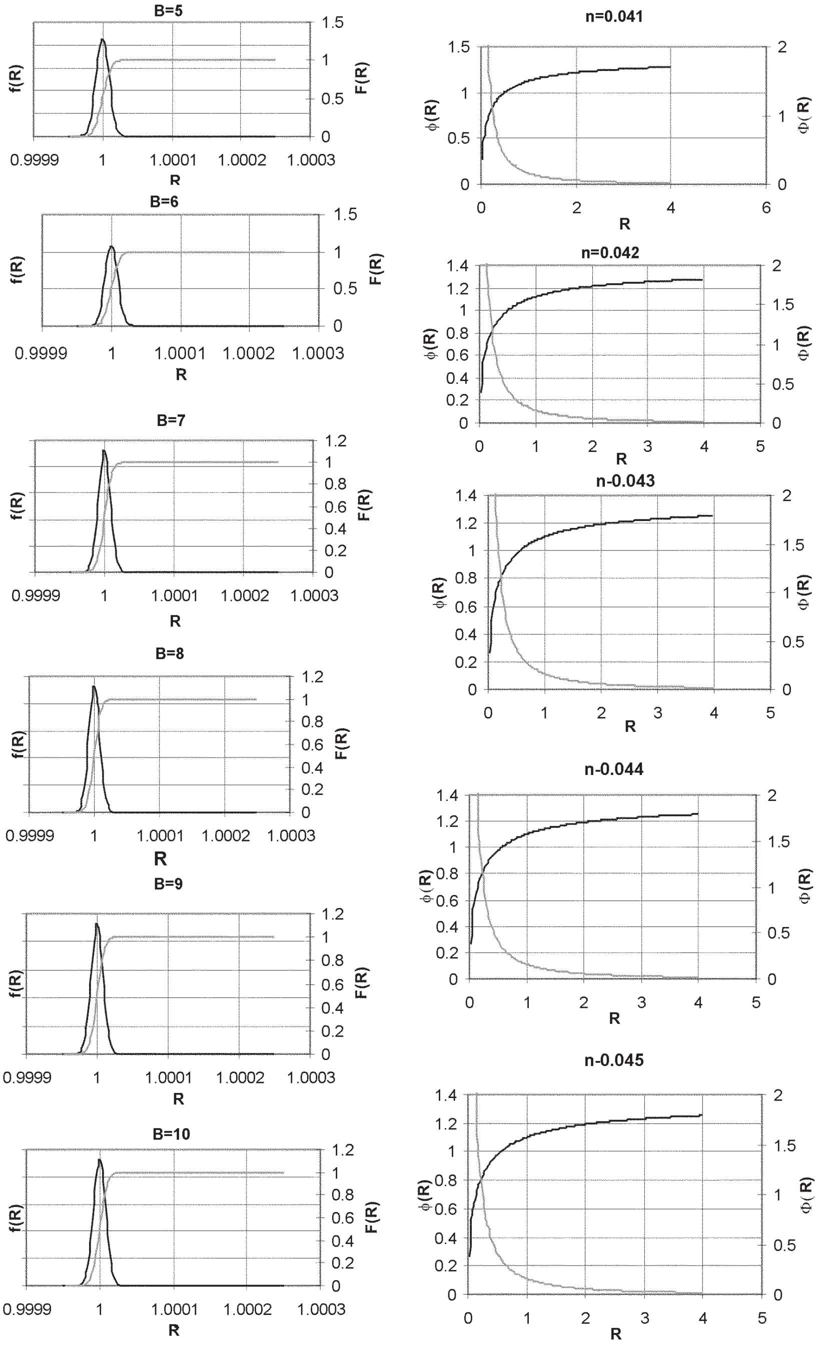

Fig. 8 Density functions and distribuants of Eq. R2: a – for normal distribution, b – for Rosin–Rammler–Sperling distribution

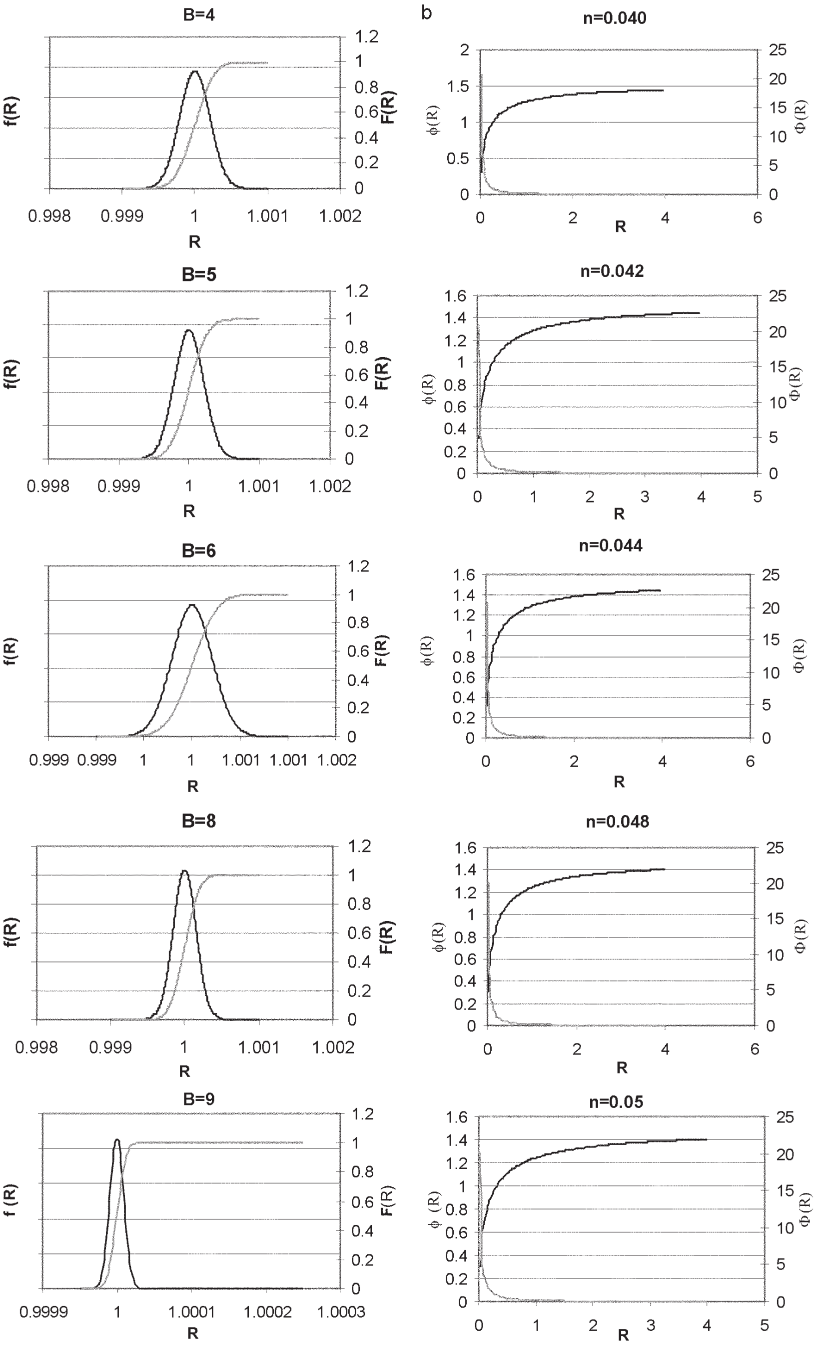

Fig. 9 Density functions and distribuants of Eq. F0: a – for normal distribution, b – for Rosin–Rammler–Sperling distribution

and density functions accept different forms for each individual value of *n* (Figs 8a, 8b, 9a and 9b).

Conclusions

Equations (2) and (3) describe very well the process of thermal dissociation of polydisperse solid materials with normal grain size distribution for the values of $B \geq 5$ – Eq. (2), and for values of $B \geq 4$ – Eq. (3). For polydisperse materials characterised by Rosin–Rammler–Sperling distribution the description is possible only in a very narrow range of θ between $\theta_1 = 0.001$ and $\theta = 0.08096$ in the case of Eq. R2, and between $\theta_1 = 0.001$ and $\theta = 0.070965$ in the case of Eq. F0. It means that these equations can only be used for very small ranges of variability of α.

Symbols

K [mm s^{-1}]
B [mm^2]
R, $\bar{R}$ [mm]
R_z, θ [–]

References

1 J. Pysiak, R. Marcinkowski and B. Podlaska, Roczniki Chemii (Polish J. of Chem.) 47 (1973) 133.
2 J. J Pysiak and Y. A. Albadwi, J. Therm. Anal. Cal., 63 (2001) 359.
3 M. Maciejewski, Thermal dissociation of solids (in Polish), Politechnika Warszawska, Warszawa 1988.
4 M. E. Brown, Handbook of Thermal Analysis and Calorimetry, Volume 1, Elsevier, Amsterdam 1998.
5 S. Bretsznajder, Problems of designing processes of chemical industry, Warszawa 1956.
6 J. Pysiak, J. Therm. Anal. Cal., 43 (1995) 9.
7 J. Pysiak, Roczniki Chemii, (Polish J. Chem.) 44 (1970) 2229.
8 J. Pysiak, B. Pacewska and E. Arciszewska, Roczniki Chemii, (Polish J. Chem.) 49 (1975) 645.
9 A. M. Ginstling and B. J. Brounshtein, Zh. Prikl. Khim., 23 (1950) 1327.
10 J. Dereń, J. Haber and R. Pampuch, Chemistry of Solids, PWN, Warszawa 1975.