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ON STOCHASTIC MODELS OF SOLID-STATE REACTIONS

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The Avrami model of solid-state reactions or transformations has frequently been presented and compared with other stochastic models. The equation often applied is shown to be merely a simplification of the full Avrami model equation (FAME). A convenient procedure for application of the FAME to the kinetics of solid-state reactions is proposed.

Several stochastic models have been proposed to describe the kinetics of phase transformations or chemical reactions in solids.

Erofeyev [1] discussed the probability of molecular events and reactions in a collection containing a large enough number of molecules to permit the use of statistics. To apply this to solid-state reactions he had to introduce a few simplifying assumptions which can never be true. For example, he neglected intercollisions between the growing nuclei of the product phase. The Erofeyev equation

$$-\ln(1-f) = k\,t^p \tag{1}$$

is the same in form as that proposed previously by Johanson-Mehl and Kolmogorov, and expresses a relation between the fractional conversion f and the reaction time t.

Mampel [2] assumed the random nucleation of the product phase grains, as well as limitation of the growth of these grains as a result of their intercollisions. Though these assumptions are quite acceptable, Mampel was not able to solve the problem. Nevertheless, in the case of spherical grains, he suggested three separate equations for the initial, the intermediate and the final stage of the reaction, respectively.

The problem seems to have been generally solved by Avrami [3]. He found a relation between the real and the idealized case, analysing all the unreal cases by Volterra methods. To prove the resulting equation, Avrami had to assume that the product grains are randomly distributed throughout the whole substrate phase, or even only throughout the transformation zone. With the additional assumption $k_g/k_n = \text{const}$, concerning the linear growth

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velocity k_g and the nucleation frequency k_n, the full Avrami model equation (FAME) was obtained [4]:

$$-\ln(1-f) = B_d F_d(x) \tag{2}$$

The functions B_d and F_d, and dimensionless time x, are defined as follows:

$$B_d = d!\, s N_o\, (k_g/k_n)^d \tag{3}$$

$$F_d(x) = (-1)^{d+1}[e^{-x} - 1 + x \ldots + (-1)^{d+1}(x^d/d!) \tag{4}$$

$$x = \int_o^t k_n\, dt \tag{5}$$

N_o is the initial concentration of active sites, d is the number of dimensions into which the grains expand, and s is the shape factor.

A few attempts have been made to develop the Avrami model by omitting the condition of constant quotient k_g/k_n. Ziabicki [5] considered mainly the crystallization of polymers. Smith and Fletcher [6] restricted their attempts to the case of metal deposition on electrodes.

Johanson–Mehl–Avrami–Kolmogorov–Erofeyev equation as simplified Avrami equation (SAE)

The FAME excludes the application of linear regression methods. Nevertheless, if the reaction time approaching zero or infinity, this equation resolves itself into the linearized equations:

$$-\ln(1-f) = \frac{n^{d+1}}{(d+1)!} B_d\, t^{d+1} = k_o\, t^{d+1} \tag{6}$$

$$-\ln(1-f) = \frac{n^d}{d!}\, B_d\, t^d = k_\infty t^d \tag{7}$$

Though k_o differs from k_∞, these two equations are usually replaced by only one, which is the same in form as the Erofeyev equation (and others). Hence, in books [7] it is called the Johanson–Mehl–Avrami–Kolmogorov–Erofeyev equation, and has been applied in a huge number of kinetic measurements, especially to describe the crystallization of polymers [8]. This

convenient equation has also been applied to polythermic measurements, and computer programs for DTG/DTA [9–11] and DSC [12] measurements have been worked out. Then, from the temperature-dependence of k, the activation energies of reactions have been determined.

However, the equation parameters k and p do not have unequivocal physical meaning. They are only the parameters of the SAE. This is the reason why, if the experiments only obey a broader range of variation of f, distinct deviation of the results from the SAE predictions is observed. From our point of view, it is much better to try to apply the FAME than to improve the consistency by fragmentation of the extent of a reaction curve, and by allowing fractional values of p, quite in opposition to the Avrami model concepts.

A proposal to apply the FAME on the basis of the Avrami model properties

A previous discussion has shown [8] that, according to the Avrami model, each kinetic curve should have an inflection point. This point is located within the borders determined by the value of d. Collections of all the possible inflection points for the particular values of d are presented in Fig. 1.

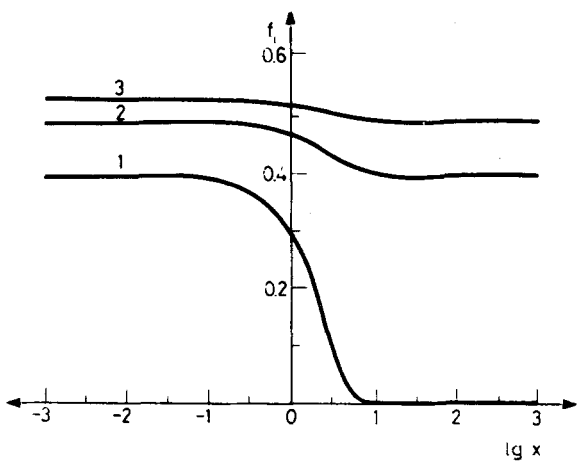

Fig. 1 Functions of f_i *vs.* $\log x_i$, representing all the possible inflection points for d = 1, 2 and 3.

The shapes of the kinetic curves depend on the rivalry parameter R:

$$R = k_n \; t_g \tag{9}$$

$$t_g = (s N_o \; k_g^d)^{-1/d} \tag{10}$$

Parameter R is a measure of the rivalry between growing grains and grains undergoing nucleation in relation to the substrate phase. Parameter t_g has the physical meaning of the unlimited growth time within which N_o grains growing without any limitation will consume a volume unit of the substrate phase.

Several examples of kinetic curves are presented in Fig. 2. The strong influence of R on the shapes of the kinetic curves is clear. The shape can vary from that of a first-order kinetic equation ($R = 0.1$) to that of a zero-order equation ($R = 40$).

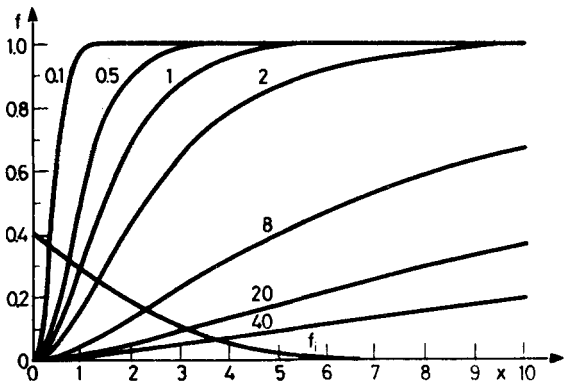

Fig. 2 Kinetic curves for d = 1, and for several values of R. The additonal curve (f_i) is drawn through the inflection points of all the possible kinetic curves.

Our proposal concerning how to apply the FAME arises from the model properties. In the first step, the coordinates of the inflection point are determined, most conveniently from the maximum in the rate *vs.* time curve. These coordinates determined d, and consequently the set of relations between all the model parameters.

These coordinates are then used as the starting point of the nonlinear optimization procedure. In this way, the values of R and k_n which give the best fitting can be found, followed by all the other model parameters. The proposed procedure is distinctly more accurate and convenient than the graphical method recommended by Delmon [13].

It should be stressed that the parameters of the FAME have physical meaning, and are measurable in another way. Such measurements have been carried out during recent months. Although not all of these experiments have been finished, the result so far obtained have always been in accordance with the predictions coming from the FAME. These studies concern the crystallization of certain polymers [8], the carbidization of iron crystallites in relation to the parasitic processes in catalysis [14], and the oxidative corrosion of calcined cokes [15].

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Zusammenfassung – Das Avrami'sche Modell von Festkörperreaktionen wurde häufig dargestellt und mit anderen stochastischen Modellen verglichen. Hier wird gezeigt, dass die häufig verwendete Gleichung eine Vereinfachung der Vollständigen Avrami'schen Modellgleichung (FAME) darstellt. Die Anwendung der FAME auf die Kinetik von Festkörperreaktionen wird vorgeschlagen und eine geeignete Verfahrensweise empfohlen.

РЕЗЮМЕ — Твердотельные реакции или превращения представлены моделью Аврами, которая сопоставлена с другими стохастическими моделями. Показано, что часто используемое уравнение Аврами является только упрощенным вариантом полного уравнения модели Аврами. Предложено применение такого уравнения к кинетике твердотельных реакций, наряду с обычным методом его применения.