RESTATEMENT AND A NEW METHOD OF APPLICATION OF THE AVRAMI MODEL

R. Dziembaj, J. Malczyk and *A. Witostawski*

FACULTY OF CHEMISTRY, JAGIELLONIAN UNIVERSITY, KARASIA 3 30-060 CRACOW, POLAND

Restatement of the Avrami equation in its nonlinear form, presentation of a convenient method of applying it, and application of the analysis to experimental results are presented. The physical meaning of the model parameters and advantages of applying the nonlinear equation are discussed.

The statistical theory of phase transformations proposed by Avrami [1] is capable of describing a wide range of complex kinetic processes. However, tractable formulas which could be easily used in experimental practice have been derived under many assumptions constraining applicability of the theory. Although some of the assumptions may not be valid for an experimental system, the most primitive form of the theory:

$$- \ln (1 - \alpha) = kt^{n} \qquad (1)$$

frequently referred to as the "Avrami equation", still continues to be used to describe the kinetics of phase transformations or chemical reactions in solids. Thus many authors announce substantial deviations between experimental results and predictions of Eq.(1). To attain better agreement with experiment, fractional values of the exponent n or variability of the parameters k and n with time t are sometimes considered. Such attempts, however, imply loss of the originally assumed physical meaning of the model parameters.

Equation (1) is only a special case of the more general equation which appeared in the Avrami paper [1] and was repeated in many books, e.g. in references [2] and [3]. Nevertheless, to the best of our knowlegde, it had not been applied to experimental data before our trial [4].

Restatement of the equation, presentation of a new, convenient method of applying it (outlined earlier in our previous work [5]) and application of the analysis to experimental results is the aim of this paper.

Restatement

Assuming a random distribution of initially present effective number N_o of "germ nuclei" per unit volume, a rate of nucleus formation according to a first-order rate law with specific rate constant k_n (the time-independent probability of formation of growth nuclei per germ nucleus per unit time), constancy of k_g (the average rate of nucleus growth in d directions) under isothermal conditions, and taking into account the relation between the actual degree of transformation and the fictitious one (free growth without any constraints) one may arrive at the kinetic equation:

$$- \ln (1 - \alpha) = d\,!\,s\,N_o\,k_g^d\,k_n^{-d}F_d (x) = B_d\,F_d (x) \tag{2}$$

$$F_d = (-1)^{d+1} \left(e^{-x} - 1 + x - \frac{x^2}{2} + ... + (-1)^{d+1} \frac{x^d}{d!} \right) \tag{3}$$

$$x = k_n t \tag{4}$$

where α stands for the fractional extent of transformation d is the number of dimensions of nucleus growth, s is a shape factor, x denotes (undimensional) time and B_d is the set of model parameters.

In all cases when x is very small (near the beginning of the transformation or k_n is very small) Eq.(2) becomes

$$-ln (1 - \alpha) = \frac{s\,N_o\,k_g^d k_n}{d + 1}t^{d+1} \tag{5}$$

and for the other extreme

$$-ln\,(\,1-\alpha\,)=sN_o\,k_g^d\,t^d \qquad (6)$$

All intermediate cases are described by Eq.(2) and equations (5-6) are only their limiting cases. Equations of the type of Eq.(1) are also obtained when the simplifying assumption is made that the rate of nucleation is constant.

Analysis

For any d Eq.(2), sigmoidal kinetic curves are obtained with one inflection point. This property is the basis of the new method of applying the equation to experimental data. Theoretically possible ordinates α_i of the inflection point are included within the intervals:

$$1-\exp\left(\frac{1}{d}-1\right)\;<\;\alpha_i\;<\;1-\exp\left(-\frac{d}{d+1}\right) \qquad (7)$$

which do not overlap and their limits are determined by the value of d. Thus, location of the inflection point (t_i, α_i) on an experimental curve determines the number d of dimensions. This diminishes the number of parameters at the initial stage of kinetic analysis.

Inserting into Eq.(2) the condition for the existence of the inflection point

$$B_d = \frac{F_{d-2}\,(x_i)}{F_{d-1}^2\,(x_i)} \qquad (8)$$

and using the identity

$$\alpha\,(t_i)=\alpha\,(x_i) \qquad (9)$$

the undimensional time x_i for the inflection point can be calculated. The property of function $F_d(x)$ that

$$\frac{\mathrm{d}F_d}{\mathrm{d}x} = F_{d-1} \qquad\qquad (10)$$

allows for the introduction of the convenient notation in Eq.(8). Following this, parameters k_n (Eq.4) and B_d (Eq.8) are readily obtained.

To avoid errors in determining k_n and B_d (from uncertainty in the location of the coordinates of the inflection point) an optimization procedure is recommended for a narrow range of the initially found values of the model parameters.

Results and discussion

The isothermal kinetics of oxygen corrosion of calcined cokes has been studied by thermogravimetry and sigmoidal curves were obtained [6]. The complex corrosion process facilitated partition of the kinetic curves near the inflection point and from a set of 16 simple kinetic equations tested, the equation $\alpha = 1-\exp(-kt)$ was found to be suitable for describing the final part of the kinetic curves. The course of the corrosion of calcined cokes was described as a stochastic nucleation and growth of the (one-dimensional)
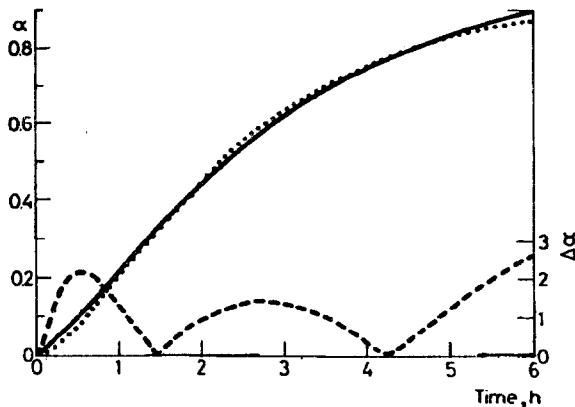

Fig.1 Results of formal optimization of Eq.(1) to experimental results of isothermal oxygen corrosion (at 835 K) of calcined cokes. (Dots - experimental values, solid line - calculated curve, and dashed line - absolute deviations $\Delta\alpha = |\,\alpha_{exp} - \alpha_{cal}\,| *10$.

channels penetrating the bulk of the cokes. This structure was confirmed by scanning electron microscopy and porosimetry [6].

The formal treatment of experimental data by Eq.(1) demands optimization of k and n values. For the kinetic data presented in Fig.1 the optimization yields $k = 0.24$, $n = 1.25$ and the nonintegral value of n considerably changing from one experiment to another.

Application of Eq.(2), according to the proposed method, for description of the kinetics of the oxygen corrosion process yields $d = 1$ in each experiment [4]. Moreover, better agreement between experimental and calculated curves over a wide range of the extent of reaction was obtained. A typical result of Eq.(2) applied to the same kinetic data is presented in Fig.2. Final values of the objective function (defined as $\sqrt{\sum (\alpha_i^{exp} - \alpha_i^{calc})^2 / l}$ where l is the total number of experimental points) are abouut three times smaller in this case.
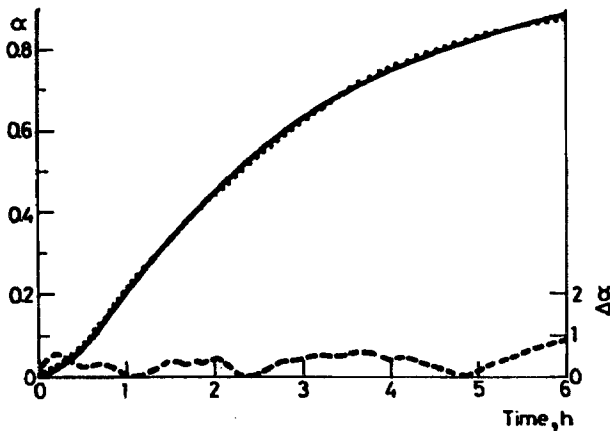

Fig.2 Typical fit of Eq.(2) to the same kinetic data ($B_1 = 0.18, k_n = 2.14$). (Dots - experimental values, solid line - calculated curve, and dashed line - absolute deviations $\Delta\alpha = |\alpha_{exp} - \alpha_{cal}| *10$.

Application of Eq.(2) preserves the physical meaning of the model parameters d, k_n, k_g defined by the theory. The first two parameters as well as B_d are determined by kinetic measurements and can then be used to characterize k_g Eq.(2):

$$k_g^d = (d!sN_o)^{-1}k_n^d B_d \tag{11}$$

The shape factor s and the initial concentration N_0 of the germ nuclei cannot be separated without additional measurements using appropriate methods of texture analysis.

Taking into account the many applications of Eq.(1) and deviations caused by this description, we expect that our findings will encourage researches to apply Eq.(2) instead of Eq.(1).

Conclusions

The Avrami model of phase transformations in its original nonlinear form Eq.(2) can be applied over the whole range of the extent of transformation, contrary to the simplified form Eq.(1) which is valid only for the very beginning or for the very end of a kinetic curve.
The parameters of Eq.(2) are defined in relation to their physical meaning. They may be separated, and determined in independent nonkinetic measurements.
The probability of nucleation results directly from the kinetic analysis and the true activation energy can be found.

References

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Zusammenfassung - Es werden die nichtlineare Form der Avrami-Gleichung und anhand eines experimentellen Beispiels ein neues geeignetes Anwendungsverfahren beschrieben. Die physikalische Bedeutung der Modellparameter und die Vorteile der Anwendung dieser nichtlinearen Gleichung werden diskutiert.