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Note

THE BOUNDARY CONDITIONS FOR KINETIC MODELS

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The problem of the validity and applicability of mathematical models in solid state kinetics is still considered a very controversial topic. Apart from the question concerning the physical meaning of the so-called "kinetic models", there are also several mathematical problems and inconsistencies in the accepted formalism. In this paper we would like to discuss the most frequently used kinetic models with respect to the boundary conditions of a rate equation.

In solid state kinetics the molar concentration of reactants is frequently replaced by the so-called degree of conversion (α) which is usually defined as [1]

$$\alpha_t = (C_t - C_0)/(C_\infty - C_0) \tag{1}$$

where C is the concentration of reactants as well as any other physical property chosen to represent the system under study. The subscripts in eqn. (1) correspond to the value at initial time ($t = 0$) and final time ($t \to \infty$), respectively. The time dependence of α is obviously expressed in the form of a differential equation

$$\mathrm{d}\alpha/\mathrm{d}t = kf(\alpha) \tag{2}$$

where k is the Arrhenius rate constant and $f(\alpha)$ is a kinetic model, i.e. an algebraic function describing the mechanism of the process.

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By integration of eqn. (2) under isothermal conditions we obtain

$$g(\alpha) = kt \tag{3}$$

where

$$g(\alpha) = \int \frac{d\alpha}{f(\alpha)} + \text{const.} \tag{4}$$

It thus follows from eqn. (1) that there are two limits for α, i.e. $\alpha = 0$ (for $t = 0$) and $\alpha = 1$ (for $t \to \infty$). As the rate constant is always finite, two boundary conditions can be derived from eqn. (3)

$$\lim_{\alpha \to 0} g(\alpha) = 0 \tag{5a}$$

$$\lim_{\alpha \to 1} g(\alpha) = \infty \tag{5b}$$

It is noteworthy that these conditions have general validity regardless of the type of kinetic model applied. Boundary condition (5a) is well known and it is used for the calculation of the constant in eqn. (4). However, boundary condition (5b) has not yet been analysed, as far as we know, and thus we will focus our attention on the discussion of its validity for the most frequently used kinetic models.

THE JOHNSON–MEHL–AVRAMI MODEL (JMA)

This model was derived for the description of nucleation growth processes. It can be expressed in a generalized form [2]

$$f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n} \tag{6}$$

and using eqn. (4) and condition (5a), an expression for $g(\alpha)$ is obtained

$$g(\alpha) = [-\ln(1-\alpha)]^{1/n} \tag{7}$$

It is evident that this equation fulfils boundary condition (5b) and thus the JMA model is consistent with respect to both the conditions defined.

THE REACTION ORDER MODEL (RO)

For the mathematical description of the processes controlled by a surface chemical reaction, the RO model is used in the form [2]

$$f(\alpha) = (1-\alpha)^n \tag{8}$$

From eqn. (4) and condition (5) it follows that

$$g(\alpha) = \begin{cases} \dfrac{1-(1-\alpha)^{1-n}}{1-n} & n \neq 1 \\ -\ln(1-\alpha) & n = 1 \end{cases} \tag{9}$$

TABLE 1

Functions $f(\alpha)$ and $g(\alpha)$ for DF models

Model	$f(\alpha)$	$g(\alpha)$
D1	$1/2\alpha$	α^2
D2	$1/[-\ln(1-\alpha)]$	$(1-\alpha)\ln(1-\alpha)+\alpha$
D3	$\dfrac{3(1-\alpha)^{2/3}}{2\left(1-(1-\alpha)^{1/3}\right)}$	$[1-(1-\alpha)^{1/3}]^2$
D4	$3/2((1-\alpha)^{-1/3}-1)$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

Boundary condition (5b) is only valid in the case of $n \geqslant 1$. This relation is equivalent to the statement that the $f(\alpha)$ function for the RO model must be either concave upwards or linear (for $n = 1$) in order to keep condition (5b). It should be pointed out, however, that the most frequently used forms of the RO model, i.e. R2 and R3 functions, correspond to $n = 1/2$ and $2/3$, respectively, and thus they do not fulfil the second boundary condition.

DIFFUSION MODELS (DF)

In the literature, there are several kinetic models for the description of such processes where the mass transport becomes rate controlling [2].

Four typical $f(\alpha)$ functions are summarized in Table 1. The corresponding $g(\alpha)$ functions were calculated using eqn. (4) and condition (5a). From this it is evident that condition (5b) is no longer valid for any of these DF models.

THE ŠESTÁK–BERGGREN MODEL (SB)

In empirical kinetics, the SB model is very popular in the form of a relatively simple equation [2–4]

$$f(\alpha) = \alpha^m (1-\alpha)^n \tag{10}$$

Unfortunately, the function $g(\alpha)$ cannot generally be written as an analytical expression because the integral defined by eqn. (4) can only be expressed explicitly in the case of integers m and n. Nevertheless, it can be shown * that condition (5a) is valid for $m < 1$ and similarly that the condition (5b) is fulfilled for $n \geqslant 1$. As the shape of the $f(\alpha)$ function can be determined

* The function $1/f(\alpha)$ for the SB model behaves as α^{-m} in the neighbourhood of 0 and as $(1-\alpha)^{-n}$ in the neighbourhood of 1. Therefore both the boundary conditions can be analysed for these special cases.

experimentally [5], it is useful to find the relationship between the above conditions and the existence of maxima (α_m) and inflex points (α_i) of the SB function, defined by the following equations

$$\alpha_m = \frac{m}{m+n} \quad m, n > 0 \tag{11}$$

$$\alpha_{i1,i2} = \frac{m \pm [mn/(m+n-1)]^{\frac{1}{2}}}{m+n} \quad m+n > 1 \tag{12}$$

By comparing eqns. (11) and (12), we see that there are in general two inflex points, i.e. $\alpha_{i1} < \alpha_m < \alpha_{i2}$. The conditions for their existence within the acceptable limits of α can be formulated

$$m \geqslant 1 \leftrightarrow \alpha_{i1} \in \langle 0, \alpha_m) \tag{13a}$$

$$n \geqslant 1 \leftrightarrow \alpha_{i2} \in (\alpha_m, 1\rangle \tag{13b}$$

According to these relationships it can immediately be seen that boundary condition (5a) is fulfilled if an inflex point α_{i1} does not exist in the interval $\alpha \in (0, \alpha_m)$. Similarly it follows that condition (5b) is only valid if an inflex point α_{i2}, defined by (13b), exists.

A particular case of the SB model is the Prout–Tompkins (PT) function [2] defined by

$$f(\alpha) = \alpha(1-\alpha) \tag{14}$$

From eqn. (4) it follows that

$$g(\alpha) = \ln\frac{\alpha}{1-\alpha} + \text{const.} \tag{15}$$

It is clear that function $g(\alpha)$ defined by eqn. (15) does not fulfil boundary condition (5a). Nevertheless, condition (5b) is still valid.

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REFERENCES

1 J. Šesták and J. Kratochvil, J. Therm. Anal., 5 (1973) 193.
2 J. Šesták, Thermophysical properties of solids, in G. Svehla (Ed.), Comprehensive Analytical Chemistry, Elsevier, Amsterdam 1984.
3 J. Šesták, G. Berggren, Thermochim. Acta, 3 (1971) 1.
4 V.M. Gorbatchev, J. Therm. Anal., 18 (1980) 194.
5 J. Málek, Thermochim. Acta, 138 (1989) 337.