Short Communication

SOME ASPECTS OF ŠESTÁK'S GENERALIZED KINETIC EQUATION IN THERMAL ANALYSIS

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It is demonstrated that Šesták's generalized kinetic equation

$$\frac{d\alpha}{dt} = k\alpha^a(1 - \alpha)^b[-\ln(1 - \alpha)]^c$$

can be transformed, for isothermal conditions, into up to three invariant expressions with two kinetic exponents. Although the integrated form of the equation

$$\frac{d\alpha}{dt} = k\alpha^a(1 - \alpha)^b$$

used to describe self-accelerating transformation processes is unknown in its general form, its particular form

$$\frac{[-\ln(1 - \alpha)]}{\alpha^a(1 - \alpha)^{b-1}} = k't$$

can be obtained as the result of the mathematical reflection of the topochemical equation $\alpha = 1 - \exp(-kt^n)$, assuming their simultaneous applicability.

Practically all kinetic equations used for mathematical modelling of solid-phase transformations under isothermal and non-isothermal conditions can be expressed by Šesták's deductive equation [1−3]:

$$\frac{d\alpha}{dt} = k\alpha^a(1 - \alpha)^b[-\ln(1 - \alpha)]^c \tag{1}$$

where the symbols are those in common use. In the general case it is *a priori* unclear what number of kinetic exponents must be used to describe a factual kinetic curve. In practice, the combination of two kinetic exponents [4] or a single exponential relationship $(1 - \alpha)^b$, where the exponent b will formally be interpreted as the order of the reaction, will in some cases be satisfactory. It is important to notice that partial modifications of the basic equation (1) may reflect the mechanisms of the solid-phase transformation in the form of the corresponding theoretical models [3, 5].

In the followings, a mathematical analysis of the basic equation (1) will demonstrate that not more than two kinetic exponents are required for the adequate

description of any experimental kinetic curve for a one-stage transformation. Let us assume that some hypothetic isothermal kinetic curve exists that is perfectly approached simultaneously by the two well-known equations [6, 7]

$$\eta = 1 - \exp{(-kt^n)} \tag{2a}$$

or, in the derived form,

$$\frac{d\eta}{dt} = nk^{\frac{1}{n}}(1 - \eta)[- \ln{(1 - \eta)}]^{1 - \frac{1}{n}} \tag{2b}$$

and

$$\frac{d\eta}{dt} = k\eta^x(1 - \eta)^y. \tag{3}$$

Here η is conversion, and the formal replacement of α by η has been done to emphasize that a hypothetic transformation is being studied. Combining equation (2b) and (3) on the basis of the accepted assumption, and using the symbol z for $\left(1 - \frac{1}{n}\right)$, we have

$$nk^{\frac{1}{n}}(1 - \eta)[- \ln{(1 - \eta)}]^{-z} = k\eta^x(1 - \eta)^y.$$

A rearrangement of the factors finally yields

$$\eta^x(1 - \eta)^{y-1}[- \ln{(1 - \eta)}]^{-z} = \text{const.} \tag{4}$$

From Eq. (4) the following generalization may be concluded: the relationship (4) with its constant right-hand part will always exist for any combination of the exponents x, $y - 1$ and $-z$. Hence, the basic equation (1) can always be transformed, utilizing Eq. (4), into three simpler invariant equations:

$$\frac{d\alpha}{dt} = k'\alpha^{a'}(1 - \alpha)^{b'} \tag{5}$$

$$\frac{d\alpha}{dt} = k''(1 - \alpha)^{b''}[- \ln{(1 - \alpha)}]^{c''} \tag{6}$$

$$\frac{d\alpha}{dt} = k'''\alpha^{a'''}[- \ln{(1 - \alpha)}]^{c'''} \tag{7}$$

The comma marks of the exponents will be omitted in the followings for simplicity's sake.

It must also be noticed that an interrelationship exists between the kinetic exponents in Eqs. (5–7), which can readily be determined from the condition $\frac{d^2\alpha}{dt^2} = 0$ in the point where the rate of the isothermal transformation is maximum.

We shall then obtain, for Eq. (5), $\sigma = \dfrac{a}{b} = \dfrac{\alpha_m}{1 - \alpha_m}$. Similarly, Eq. (6) yields

$\beta = \dfrac{b}{c} = \dfrac{1}{[-\ln(1 - \alpha_m)]}$, and Eq. (7) $\mu = \dfrac{a}{c} = \dfrac{\alpha_m}{(1 - \alpha_m)\ln(1 - \alpha_m)}$. By means of these relationships, Eqs (5, 6, 7) can be written with one single unknown kinetic exponent, since the values of σ, β and μ can relatively easily be established from the experimental kinetic curve. Thus, after all simplifications are carried out, the final form obtained is

$$\frac{d\alpha}{dt} = K\alpha^{\sigma b}(1 - \alpha)^b \tag{8}$$

$$\frac{d\alpha}{dt} = K(1 - \alpha)^{\beta c}[-\ln(1 - \alpha)]^c \tag{9}$$

$$\frac{d\alpha}{dt} = K\alpha^{\mu c}[-\ln(1 - \alpha)]^c. \tag{10}$$

The experimental determination of the remaining unknown kinetic exponent may be carried out by the method proposed by us in [7]. If the rate of transformation under isothermal conditions is expressed by $\dfrac{d\alpha}{dt} = h\kappa$, where h is the heigth of the corresponding point on the differential curve, and κ is a proportionality coefficient, then the above equations, after logarithmation, will yield

$$\ln h = b \ln\left[\alpha^{\sigma}(1 - \alpha)\right] + \ln\frac{K}{\kappa}$$

$$\ln h = c \ln\left\{(1 - \alpha)^{\beta}[-\ln(1 - \alpha)]\right\} + \ln\frac{K}{\kappa}$$

$$\ln h = c \ln\left\{\alpha^{\mu}[-\ln(1 - \alpha)]\right\} + \ln\frac{K}{\kappa}.$$

If an idealized diagram is constructed from the experimental data, the kinetic exponents b and c to be determined can be calculated from the slopes of the straight lines.

For the mathematical modelling of the kinetics of self-accelerating processes under isothermal conditions, the modification of the starting equation (1) to the following form is of greatest interest (Eqs (5) and (8)):

$$\frac{d\alpha}{dt} = K\alpha^a(1 - \alpha)^b = K\alpha^{\sigma b}(1 - \alpha)^b.$$

In the general case the value of the kinetic exponent a does not exceed 1, while that of the exponent b varies within wider limits [5]. Obviously, the utilization of this equation is of greatest importance to describe the acceleration process itself,

since the knowledge of the kinetic exponent a allows a quantitative evaluation of the effect of the newly formed product or of an intermediate activating complex on the overall rate of reaction.

The integrated form of the equation $\dfrac{d\alpha}{dt} = K\alpha^a(1 - \alpha)^b$ is not known in the literature. An accurate integration is possible only if the values of a and b are known whole numbers [8], that is, wide utilization in practice of this equation is excluded. Based on the general concept of operation computations, we shall attempt to find an integrated form of Eq. (5) in the shape of the mathematical reflection of the well-known exponential equation $\alpha = 1 - \exp(-kt^n)$ in its derived form $\dfrac{d\alpha}{dt} = nkt^{n-1}(1 - \alpha)$. Putting them equal in the equality $K\alpha^a(1 - \alpha)^b = nkt^{n-1}(1 - \alpha)$ and performing some simple transformations, the final form obtained is

$$\frac{[-\ln(1 - \alpha)]}{\alpha^{\sigma a}(1 - \alpha)^{b-1}} = \frac{K}{n}t = K't \tag{11a}$$

or, if the ration $\sigma = \dfrac{a}{b}$ is already known,

$$\frac{[-\ln(1 - \alpha)]}{\alpha^{\sigma b}(1 - \alpha)^{b-1}} = K't. \tag{11b}$$

If, however, the accurate determination of σ is impossible owing to the very slight slope of the kinetic curve, the above relationships can be established by the help of the equation

$$\sigma = \frac{\ln\dfrac{1 - \alpha_1}{1 - \alpha_2}}{\ln\dfrac{\alpha_2}{\alpha_1}} \tag{12}$$

where α_1 and α_2 are conversions at the same height of the peak section of the differential kinetic curve, i.e. when $\left(\dfrac{d\alpha}{dt}\right)_1 = \left(\dfrac{d\alpha}{dt}\right)_2$. From Eq. (12) one can readily obtain the valuable relationship

$$\alpha_m = \frac{\ln\dfrac{1 - \alpha_1}{1 - \alpha_2}}{\ln\dfrac{\alpha_2}{\alpha_1} + \ln\dfrac{1 - \alpha_1}{1 - \alpha_2}} \tag{13}$$

The integrated form of Eq. (5) may prove extremely valuable to find the kinetic exponents a and b within the conversion interval α_x and α_y of interest, using the

following relationship:

$$\frac{[-\ln(1-\alpha_x)\alpha_y^{\sigma b}(1-\alpha_y)^{b-1}]}{\alpha_x^{\sigma b}(1-\alpha_x)^{b-1}[-\ln(1-\alpha_y)]} = \frac{t_x}{t_y} \ . \tag{14}$$

Finally, it should be noted that the integrated equation (11) is a specific reflected function of the topochemical equation $\alpha = 1 - \exp(-kt^n)$, this leading to the necessity that a linear anamorphose in the form of $\ln[-\ln(1-\alpha)] = n\ln t + \ln k$ must exist.

References

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