Short Communication

SOME SUGGESTIONS FOR IMPROVING THE UTILIZATION OF THE FUNCTION $g(\alpha)$ AND $p(x)$ TO IDENTIFY THE MECHANISM OF A THERMAL TRANSFORMATION

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The procedures allowing improvement of utilizing the known functions $g(\alpha)$ and $p(x)$ in the kinetics of non-isothermal transformations are analyzed.

I. The method developed by Šestak, Šatava, Škvara, Berggren and Wendlandt [1—6] is frequently used in the practice of kinetics studies based on experimental data from thermal analysis. This method consists in the computerized selection of the best linearization for the series of functions $\ln g_i(\alpha)$ *vs.* $1/T$, in conformity with the equation

$$\ln g(\alpha) - \ln p(x) = \ln \frac{AE}{R\beta} \tag{1}$$

This implies the assumption that the relationship $\ln p(x)$ *vs.* $1/T$ is linear. This assumption, however, is not fully correct, and hence may introduce some distortion in the selection of the function $g(\alpha)$ and the limits of its applicability regarding the conversion value α. Let us write the known kinetic equations for non-isothermal kinetics:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{2}$$

$$g(\alpha) = \frac{AE}{R\beta} p\left(\frac{E}{RT}\right) \tag{3a}$$

where

$$p(x) = p\left(\frac{E}{RT}\right) = \frac{\exp\left(-\frac{E}{RT}\right)}{\left(\frac{E}{RT}\right)^2} \left[1 - \frac{2!}{\frac{E}{RT}} + \frac{3!}{\left(\frac{E}{RT}\right)^2} - \cdots\right]$$

and

$$p\left(\frac{E}{RT}\right) = \left(\frac{RT^2}{E}\right)^2 \exp\left(-\frac{E}{RT}\right) \Delta p\left(\frac{E}{RT}\right) \tag{4}$$

respectively. Let us substitute Eq. (4) into Eq. (3a). This will yield

$$g(\alpha) = \frac{ART^2}{E\beta} \exp\left(-\frac{E}{RT}\right) \Delta p\left(\frac{E}{RT}\right)$$ (3b)

It may be demonstrated that the factor $\Delta p(E/RT)$ is practically independent of temperature. Hence, according to [7] and [8], the function $\Delta p(x)$ can be expressed in the form of the relationships

$$\Delta p(x) = \frac{x}{x+2} \quad \text{and} \quad \Delta p(x) = \frac{1}{\sqrt{1 + \frac{4}{x}}}$$

Then

$$\frac{d\Delta p(x)}{dT} = \frac{2R}{(E + 2RT)^2}$$ (5)

and the value of the right-hand side of this equation is close to zero. For instance, at $E = 100$ kJ/mol and $T = 500$ K, the value of $\frac{d\Delta p(x)}{dT}$ is $1.4 \cdot 10^{-9}$.

Consequently, for more accurate kinetic computations the starting equation (1) should be applied in the form

$$\ln\left[\frac{g(\alpha)}{T^2}\right] - \ln \hat{p}(x) = \ln \frac{AR}{E\beta}$$ (6)

where

$$\hat{p}(x) = \exp\left(-\frac{E}{RT}\right) \Delta p\left(\frac{E}{RT}\right)$$

II. In the cited method for identifying the mechanism function of the transformation in question [1–6], the function $f(\alpha) = (1 - \alpha)^n$ is used to describe the reaction of the boundary between phases, and in the computerized calculations the following kinetic exponents are used: $n = 0; 1/3; 1/2; 2/3; 1$. This appears unfounded, however, since in reality the topochemical transformation may proceed at intermediate kinetic orders too. In addition, studies [9] have demonstrated that realistic physicochemical processes with $n > 1$ must also be considered. In our opinion, at the present stage of development of computers one should not be satisfied with a *priori* values of the kinetic exponent n, but should find them from a corresponding mathematical processing of the thermoanalytical curves. In the following, the routes of analytical computations will be outlined, starting from the kinetic parameters

$$g(\alpha) = \frac{1 - (1 - \alpha)^{1-n}}{1 - n} = \frac{ART^2}{E\beta} e^{-\frac{E}{RT}} \Delta p\left(\frac{E}{RT}\right)$$ (7)

and

$$A = \frac{(1 - \alpha_p)^{1-n}}{n} \frac{E}{RT_p^2} \exp\left(\frac{E}{RT_p}\right)$$ (8)

At the point of maximum rate of transformation at the temperature T_p, Eqs (7) and (8) can be united to yield finally

$$\frac{[1 - (1 - \alpha_p)^{1-n}]n}{(1 - n)(1 - \alpha_p)^{1-n}} = \Delta p \left(\frac{E}{RT_p}\right) \tag{9}$$

If the temperature integral is solved according to [7], one obtains

$$\frac{[1 - (1 - \alpha_p)^{1-n}]n}{(1 - n)(1 - \alpha_p)^{1-n}} = \frac{E}{E + 2RT_p} = \lambda \tag{10}$$

At the value $\lambda = 1$, Eq. (10) is identical with the known equation of Horowitz and Metzger [10]: $1 - \alpha_p = n^{\frac{1}{1-n}}$; at $\lambda = 0.94$ one obtains the Gyulai–Greenhow equation [11]: $1 - \alpha_p = 1.062\, n^{\frac{1}{1-n}}$. Under realistic conditions, the experimental value λ can obviously have different values depending on E/RT_p. Equation (10) can simply be transformed into

$$1 - \alpha_p = \left[1 + \frac{1-n}{n}\left(\frac{x_p}{x_p + 2}\right)\right]^{\frac{1}{1-n}} \tag{11}$$

Let us consider a numerical example: $E = 84$ kJ/mol, $T_p = 500$ K; then $x_p = 0.91$, $\alpha_p = 0.5$. The calculation according to Horowitz and Metzger yields $n = 2$, and according to Gyulai and Greenhow $n = 1.72$, whereas Eq. (11) yields $n = 1.6$.

III. In the cited method of kinetic studies [1–6], when processes with nucleus formation and subsequent growth of nuclei are being modelled, the following functions are utilized for the mechanism of the process:

$$g(\alpha) = (1 - \alpha)[- \ln(1 - \alpha)]^{1 - \frac{1}{n}} \tag{12}$$

and

$$f(\alpha) = [- \ln(1 - \alpha)]^{\frac{1}{n}} \tag{13}$$

These equations arose from differentiation of the well-known topochemical equation of Kolmogorov, Erofeev, Kazeev, Avrami and Mampel:

$$- \ln(1 - \alpha) = kt^n \tag{14}$$

After its differentiation in the cited mode, one obtains

$$\frac{d\alpha}{dt} = nkt^{n-1}(1 - \alpha) \tag{15}$$

However, if the starting equation is differentiated in another form:

$$\ln\left[-\ln\left(1-\alpha\right)\right] = n \ln t + \ln k$$

another expression will be obtained:

$$\frac{d\alpha}{dt} = \frac{n}{t}\left(1-\alpha\right)\left[-\ln\left(1-\alpha\right)\right] \tag{16}$$

in which the rate constant k is absent (since under isothermal conditions $d \ln k/dt = 0$). If the starting equation (14) is substituted into Eq. (16), one finally obtains a third differential equation for isothermal conditions:

$$\frac{d\alpha}{dt} = nk^{\frac{1}{n}}\left(1-\alpha\right)\left[-\ln\left(1-\alpha\right)\right]^{1-\frac{1}{n}} \tag{17}$$

which is actually utilized by the authors of [1–6] in the separation of the functions $g(\alpha)$ and $f(\alpha)$. However (as made obvious by the mode in which Eq. (17) was derived), this equation can only be used to describe isothermal processes. Strictly speaking, therefore, it is only the differential kinetic equation Eq. (15) that may be used to describe the nucleus formation and nucleus growth process under non-isothermal conditions. This circumstance must be taken into account in the correction of the corresponding computer programs.

References

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