Short Communications

SOME OBSERVATIONS REGARDING THE COMPENSATION EFFECT OBSERVED IN THE KINETICS OF NON-ISOTHERMAL TRANSFORMATIONS

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A kinetic equation is analyzed whose application in practice for a number of transformations will demonstrate the linear correlation between activation energy and ln A (the preexponential factor in the Arrhenius equation).

In the general case there is no doubt of the truth of the effect well known in chemical kinetics the compensation relationship of the parameters in the Arrhenius equation in the shape of the linear equation $\ln A = E/RT_x + \ln k_x$ [1], where T_x and $\ln k_x$ are the coordinates of the isokinetic point in the set of lines $\ln k$ vs. $1/T$. Under non-isothermal experimental conditions, however, a compensation effect sometimes appears in the form of the empirical equation $\ln A = aE + b$, although obviously this set of lines $\ln k$ vs. $1/T$ have no common intersecting point. Formally, an apparent isokinetic temperature may be computed from the relationship $a = 1/RT_x$. This form of the compensation effect has recently been described by Dollimore and Taylor [2] and needs some additional explanation.

In the general case, the rate of a one-stage irreversible transformation in its generalized form can be described by the model

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{1}$$

where the function $k(T)$ is usually equalized to the Arrhenius equation $k = A \exp(-E/RT)$. We shall not specify here the function $f(\alpha)$ and the rate of heating $q = \mathrm{d}T/\mathrm{d}t$. At the point of maximum transformation rate one can obtain from the well-known condition $\left(\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2}\right)_m = 0$

$$f(\alpha)_m \frac{Eq}{RT_m^2} + f'(\alpha)_m \left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_m = 0 \tag{2}$$

Substituting Eq. (1) into Eq. (2) and carrying out some mathematical transformations, one finally obtains

$$A = -\frac{Eq}{RT_m^2 f'(\alpha)_m} \exp\left(+\frac{E}{RT_m}\right) \tag{3}$$

Even a simple visual inspection of Eq. (3) reveals that the kinetic parameters E and A, in the general case, are functionally related and that, for some states of the series of reaction systems, a linear relationship between $\ln A$ and E is possible. Let us write Eq. (3) in the logarithmic form:

$$\ln A = \frac{E}{RT_m} + \ln\left(\frac{-Eq}{RT_m^2 f'(\alpha)_m}\right) \tag{4}$$

If in the investigated series of transformations it happens that – at constant q – the temperatures T_m are very close to one another, and the term $\ln\left(\frac{-Eq}{RT_m^2 f'(\alpha)_m}\right)$ depends only slightly on E, then, after differentiation, one obtains

$$\frac{\mathrm{d}\ln A}{\mathrm{d}E} = \frac{1}{RT_m} + \frac{1}{E} \tag{5}$$

Since $\frac{1}{RT_m} \gg \frac{1}{E}$ in almost all cases, formally the plot $\ln A$ vs. E will yield some straight correlation, though in fact the relationship is not linear. This correlation is shown in Fig. 1. It may be seen from the Figure that this compensation effect,

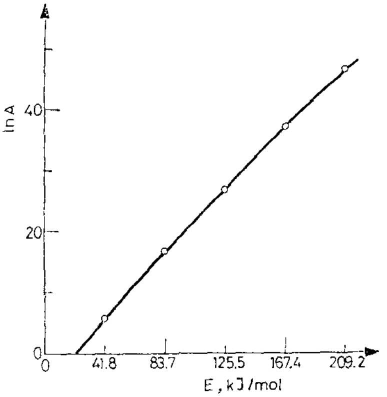

Fig. 1. Graphical representation of the compensation effect according to the equation $\ln A = E/RT_m + \ln Eq/RT_m^2$; $q = 60°/\mathrm{min}$; $T_m = 500$ K; $f'(\alpha)_m = \frac{(1-\alpha_m)^{1-n}}{n} \simeq 1$, when $f(\alpha) = (1-\alpha)^n$.

strictly speaking, must be considered an apparent phenomenon only, since there is no common isokinetic point of the coordinates.

In thermoanalytical practice, the compensation often takes place for irreversible chemical reactions which are formally considered as simple one-stage transformations, but are in fact the sum of at least two parallel independent reactions. By way of example, one may cite the oxidation of diamonds [3–5]. We have stated earlier [6] that, depending on the experimental conditions the oxidation of various diamond materials (single crystals or powders) yields a mixture of CO_2 and CO in various ratios. Consequently, the overall chemical reaction should be described in the general case by the following kinetic equation:

$$\frac{d\alpha}{dt} = \lambda_1 k_1 (1-\alpha)^{n_1} + \lambda_2 k_2 (1-\alpha)^{n_2} \tag{6}$$

where $\lambda_1 + \lambda_2 = 1$. The ratio λ_1 to λ_2 depends, in the general case, on the experimental conditions, on the dispersed state of the starting material and on the diffusion coefficients. With the condition $n_1 \simeq n_2$, Eq. (6) may be written in the form

$$\frac{d\alpha}{dt} = (\lambda_1 k_1 + \lambda_2 k_2)(1-\alpha)^n \tag{7a}$$

or

$$\frac{d\alpha}{dt} = k_{\text{eff}}(1-\alpha)^n . \tag{7b}$$

Hence, if at a kinetic analysis of the composition transformation of the material, if Eq. (7b) is used, then it will yield certain effective values E_{eff} and A_{eff}, i.e.

$$A_{\text{eff}} \exp\left(\frac{-E_{\text{eff}}}{RT}\right) = \lambda_1 A_1 \exp\left(\frac{-E_1}{RT}\right) + \lambda_2 A_2 \exp\left(\frac{-E_2}{RT}\right). \tag{8}$$

In the range of low conversions, at a certain temperature T_0, the identity $A_1 \exp(-E_1/RT_0) \equiv A_2 \exp(-E_2/RT_0)$ may exist. Then Eq. (8) will take the form

$$A_{\text{eff}} \exp(-E_{\text{eff}}/RT_0) = A_1 \exp(-E_1/RT_0) = A_2 \exp(-E_2/RT_0).$$

If the characteristic temperature T_0 appears in the capacity of the isokinetic temperature T_x, the model assumed in the present paper will in fact turn into the equation of the compensation effect:

$$\ln A_{\text{eff}} = E_{\text{eff}}/RT_0 + \ln k_{\text{eff}}(T_0). \tag{9}$$

According to [5], in the oxidation of synthetic diamonds the isokinetic temperature is actually in the range of low conversions.

The question of compensation effects in reversible chemical reactions has been discussed in [7].

References

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