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INTERPRETATION OF THE DEPENDENCE OF THE EFFECTIVE VALUES OF KINETIC PARAMETERS ON THE DEGREE OF TRANSFORMATION

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ABSTRACT

It has been shown that the observed dependence of the activation energy, calculated by means of isoconversional methods, on the degree of transformation is often only an apparent effect. The existence of this dependence may be easily interpreted within the framework of the commonly used speed equation as the violation of the similarity of the kinetic curves, obtained at different heating rates, as a result of the complex character of the process. An approach has been proposed which permits us to describe each kinetic curve from the series of dissimilar curves by the pair of kinetic parameters which do not depend on the degree of transformation, but do depend on the heating rate. With the help of this approach the violation of the similarity may be revealed directly. It has also been noted that the dependence of the activation energy on the degree of transformation disappears when describing the process in terms of the parallel reaction model.

The authors of refs. 1–3 showed that the effective values of the kinetic parameters of calcium oxalate monohydrate dehydration, calculated with methods using a constant value of the degree of transformation (according to ref. 4 they are called isoconversional), depend on α. Thus, the activation energy E decreases within the interval 150–70 kJ mol^{-1} with an increase in α. The existence of the dependence of E on α is explained [1,2] by the complex character of the dehydration which consists of at least two parallel processes. In ref. 3 an attempt was made to take into consideration the dependence of E on α in explicit form. This led to a new speed equation [3,5] different from that commonly used

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{1}$$

where T is absolute temperature, β is the heating rate, $f(\alpha)$ is the formal model of the process, R is the gas constant and A is the pre-exponential factor.

The dependence of E on α is mentioned in other references as well, and we consider that it is necessary to analyse the dependence from the view-point of the main statements of non-isothermal kinetics. Our paper shows that the dependence of the kinetic parameters on the degree of transformation which is sometimes observed when using isoconversional methods, is an apparent effect and can easily be interpreted within the framework of eqn. (1).

For any isoconversional calculation method the following equation (or its integral anamorphose) is valid

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{ij}\beta_i = \ln\left[Af(\alpha_j)\right] - \frac{E}{RT_{ij}} \tag{2}$$

where α_j, T_{ij} are the coordinates of the j-th point on the i-th kinetic curve corresponding to the heating rate β_i. The degree of decomposition α_j in eqn. (2) is the same for all heating rates. Equation (2) is valid only when $f(\alpha)$ does not depend on the heating rate, in other words when the kinetic curves obtained at different heating rates are similar. Reference 6 is devoted to the detailed analysis of the similar kinetic curves obtained in non-isothermal conditions and therefore we will not deal with this question in this paper.

From a mathematical point of view similarity of two non-isothermal kinetic curves m and n means that they can be transformed into each other with the help of a linear transformation of temperatures

$$T_{\mathrm{m}j} = a_{\mathrm{mn}}T_{\mathrm{n}j} + b_{\mathrm{mn}} \tag{3}$$

Equation (3) is valid for any values of α_j. The violation of the similarity of the kinetic curves corresponding to different heating rates leads to the violation of equality in eqn. (3). For the transformation of the dissimilar kinetic curves into each other it is necessary to introduce the dependence on α_j into eqn. (3)

$$T_{\mathrm{m}j} = a_{\mathrm{mn}}(\alpha_j)T_{\mathrm{n}j} + b_{\mathrm{mn}}(\alpha_j) \tag{4}$$

To determine the influence of the violation of the similarity of the kinetic curves on the kinetic parameters obtained by means of the isoconversional method, let us rewrite eqn. (1) in the integral form, preserving the condition of the formal model, i.e. a constant process: $g(\alpha_j) = \text{constant}$ at all β_i

$$g(\alpha_j) = \frac{A}{\beta_i}\int_0^{T_{ij}} \exp\left(-\frac{E}{RT}\right)\mathrm{d}T = \text{constant} \tag{5}$$

It is clear that if the curves corresponding to different β_i are similar then the upper limit of the integral (eqn. (5)) will be given by eqn. (3) and eqn. (5) will be valid for all α_j with constant values of E and A.

If the similarity of the curves is violated, the condition $g(\alpha_j) = \text{constant}$ cannot be satisfied at all β_i as $g(\alpha)$ becomes a function of the heating rate. However, isoconversional methods presuppose that eqn. (5) is true, i.e. kinetic curves corresponding to different heating rates are similar. As a result of this, the calculation of the effective values of kinetic parameters by means of the dissimilar kinetic curves is fulfilled as if the latter are similar. It is evident that preservation of equality in eqn. (5) may be gained only at the expense of the violation of the constancy of A and E as there are no other parameters in eqn. (5). The non-constancy of the parameters A and E as a result of the violation of similarity leads to two effects which are described below.

First, for each constant α_j value there will be a definite number of temperatures $T_{ij}^{\star}$ differing from the corresponding similar row of temperatures T_{ij}. This is why kinetic parameters calculated by means of the isoconversional method will depend on the temperature interval for which they were calculated. This effect is stronger, the larger the range of heating rates β_i used.

Secondly, when changing the α_j value the upper limit of the integral (eqn. (5)) for dissimilar curves will be given by eqn. (4). As a result of the dependence of the upper limit of the integral on α the ultimate realisation of eqn. (5) leads to an apparent dependence of the effective value of the activation energy on the degree of transformation.

It should be stressed that both effects mentioned above (the dependence of the kinetic parameters on the temperature interval at one and the same degree of transformation α_j, and the dependence of the kinetic parameters on α_j) are apparent, or secondary effects. They have the same general cause, i.e. the violation of the similarity of the kinetic curves when the heating rate changes. In fact, these effects mask the violation of similarity which may be revealed in the form of the dependence of the effective values of the parameters A and E (corresponding to a certain kinetic curve) on the heating rate. Let us consider this problem in more detail.

Here, the parameters corresponding to a kinetic curve are the parameters which can be found as a solution of the equation

$$\sum_{j=1}^{k}\left[g(\alpha_j) - \frac{1}{\beta}\int_0^{T_j}\exp\left(-\frac{E}{RT}\right)\,\mathrm{d}T\right]^2 = \min \tag{6}$$

$g(\alpha_j)$ in eqn. (6) is substituted by one of the well-known approximation methods, e.g. in the form of L-th power row

$$g(\alpha) = \sum_{l=0}^{L} a_l\alpha^l \tag{7}$$

It is evident that parameter E in eqn. (6) may be obtained with an accuracy limited only by the quality of the experiment. However, it is impossible to calculate parameter A from eqn. (6). Nevertheless, A can easily be obtained from the apparent compensation effect

$$\log_{10} A = aE + b \tag{8}$$

by substituting the E value acquired from eqn. (6) in eqn. (8). Values a and b in eqn. (8) are the parameters of the linear regression for which the set of $\log_{10}$ A and E values can be obtained by any method of calculation of kinetic parameters based on the variation of the process model in its explicit form [7]. Consequently, any kinetic curve can be described by the pair of kinetic parameters obtained as the solution of eqns. (6)–(8). If eqn. (7) is equally accurate for all parts of the kinetic curve, these parameters will not depend on either the temperature interval for α. This means that when using the formal-kinetic method of calculation of kinetic parameters it is impossible to discover any real dependence of the kinetic parameters on the degree of transformation.

Thus, the violation of the similarity of the kinetic curves obtained at different heating rates manifests itself in the dependence of $g(\alpha)$ on β. As a result the coefficients of eqn. (7) become a function of the heating rate which, in its turn, leads to the dependence of E and A on β calculated by eqns. (6)–(8). Consequently, the violation of the similarity of the kinetic curves (manifesting itself in the case of isoconversional methods in the form of the above-mentioned secondary effects: dependence of E on α, and dependence of E on the temperature interval) may be revealed directly in the form of the dependence of the kinetic parameters on the heating rate (by means of eqns. (6)–(8)).

Considering the proposition of refs. 3 and 5 for the substitution of eqn. (1) by an alternative form (taking into consideration the dependence of E on α) we shall stress that the substitution of the base equation (eqn. (1)) may be justified only in such a case when the latter cannot describe some essential effect. From this point of view the proposed substitution in refs. 3 and 5 does not have sufficient grounds for two reasons. First, the dependence of E on α is a secondary (apparent) effect. Secondly, such dependence (as was shown earlier) may be explained without substitution of the all-accepted eqn. (1). The apparent dependence of the effective value of the activation energy on the degree of transformation can be eliminated with the help of eqn. (1) by establishing the concrete cause of the violation of the similarity of the kinetic curves obtained at different heating rates. As similarity of kinetic curves is characteristic only of processes which can be considered, at least formally, as one-stage processes (processes with a clearly manifested limiting stage, competitive processes with similar values of activation energy, etc.) the most probable cause of violation of similarity is the complex character of the process.

We should recollect here that the effect of the activation energy (obtained by means of the isoconversional method) on the degree of transformation was observed [8] for model data corresponding to two competitive parallel processes with different activation energies. Therefore, one of the possible ways of eliminating the apparent effect of the dependence of E on α is a transition to the parallel reaction model

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \sum_i k_i f_i(\alpha) \tag{9}$$

TABLE 1

Formal models and kinetic parameters of the dehydration process of calcium oxalate monohydrate decribed as two parallel reactions (indices 1 and 2)

Reference	$f_1(\alpha)$	E_1 (kJ mol^{-1})	A_1 (min^{-1})	$f_2(\alpha)$	E_2 (kJ mol^{-1})	A_2 (min^{-1})
1	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	168.2	2.0×10^{22}	$2(1-\alpha)^{1/2}$	69.2	4.7×10^{7}
1	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	167.5	2.0×10^{22}	$2(1-\alpha)^{1/2}$	70.2	6.3×10^{7}
2	$(1-\alpha)$	189.0	4.6×10^{22}	$2(1-\alpha)^{1/2}$	86.0	2.5×10^{9}

where k_i and $f_i(\alpha)$ are, respectively, the rate constant and the formal model of the i-th process. Thus, in refs. 1 and 2 calcium oxalate monohydrate dehydration was successfully described as two parallel processes. The results of the calculations obtained in these references are presented in Table 1 (in ref. 1 two variants of the description are recommended as equally suitable).

Taking into consideration the inevitable difference in the samples of calcium oxalate monohydrate used by the researchers [1,2] and the difference in the approaches used to describe dehydration, the values of the kinetic parameters are in good agreement and the parallel process models are of the same type. Such agreement between independently obtained results is undoubtedly a serious argument in favour of the correctness of the approaches proposed in refs. 1 and 2.

Thus, the observed dependence of the effective value of the activation energy (obtained by isoconversional methods) on the degree of transformation may be interpreted within the framework of eqn. (1) as an apparent effect, due to the violation of the similarity of the kinetic curves. It may be eliminated when describing the process in terms of the parallel reaction model.

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