A METHOD OF COMPARING KINETIC CURVES OBTAINED UNDER ISOTHERMAL AND NONISOTHERMAL CONDITIONS

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ABSTRACT

The possibilities of comparing kinetic curves obtained under isothermal and nonisothermal conditions are considered with the aim of elucidating the influence of experimental conditions on the mechanism of the process. It is shown that the affinitive transformations used in isothermal and nonisothermal kinetics are not identical, and lead to curves which cannot be compared one with another. A special method of comparing kinetic curves is proposed. This method relies on analyzing the shape of the affinitively transformed isothermal kinetic curve and the nonisothermal one previously reduced to the isothermal form. The results of testing the proposed method on model data prove its efficiency.

INTRODUCTION

Comparison of the results of kinetic processing of data obtained under isothermal and nonisothermal experimental conditions is a source of information about the mechanism of the process. As a rule, the values of the kinetic parameters are compared. It is obvious that such comparison can yield only information about the difference of the temperature dependences of the rate of the process proceeding under isothermal and nonisothermal conditions. Of no less interest is information about the influence of the regime of the kinetic experiment on the mechanism of the process. On the face of it, such information can be obtained by comparing the mathematical models of the process which describe it in the best way. In practice, however, the process models, owing to the fundamental ambiguity [1] of their choice, are not directly associated with the mechanism. It would therefore be wrong to consider their difference as a reliable criterion of the change in the mechanism taking place in going from one experimental regime to another. Below we consider a simple method of comparing kinetic curves, on the basis of which one can obtain information about the change in the mechanism of the process caused by a change in the experimental conditions.

To determine the possible change in the mechanism of a process caused by a temperature change, in isothermal kinetics the affinitive transformation [2] of kinetic curves (transformation degree–time) is normally used. This transformation is carried out by introducing the quantity of reduced time, which is the ratio of the reaction time to the time of reaching a given degree of transformation (usually 0.5 or 0.9). The shape of affinitively transformed curves is determined solely by the mechanism of the process, and is independent of the temperature and the values of the kinetic parameters. Thus, the difference in shape observed in comparing affinitively transformed kinetic curves corresponding to different experimental temperatures points to the possible change in the mechanism of the process caused by the temperature change.

In Ref. 3, affinitive transformation for nonisothermal kinetic curves (transformation degree–temperature) was proposed. By analogy with the affinitive transformation of isothermal curves, in this case the value of reduced temperature is introduced. The shape of the kinetic curves resulting from such transformation does not depend on the heating rate and the kinetic parameters of the process, and is determined solely by its mechanism. However, the affinitively transformed nonisothermal curves are far less sensitive [1] to the mechanism of the process compared with the isothermal ones, which impedes their widespread use.

It should be noted that the affinitively transformed isothermal and nonisothermal kinetic curves cannot be compared, since they represent dependences of the transformation degree on different physical quantities. A lame attempt at such comparison was made in Ref. 4, where nonisothermal curves were reduced to the "isothermal" form by transforming temperature to time through its division by the heating rate, after which the obtained curve was considered as an affinitively transformed isothermal one and was compared to the affinitively transformed kinetic curve obtained in the isothermal regime. Let us explain why such a comparison cannot be considered as correct.

It was noted above that the main property of the affinitively transformed kinetic curve is the fact that its shape is determined solely by the mechanism of the process. This property follows [2] from the possibility of separating the variables (in other words, from their independence) in the equation

$$d\alpha/dt = k(T)f(\alpha) \tag{1}$$

where $d\alpha/dt$ is the rate of the process, T is temperature, α is the transformation degree, $k(T)$ is the rate constant, and $f(\alpha)$ is the process model. The use of eqn. (1) for describing data obtained under nonisothermal conditions, in which not only the transformation degree but also the temperature is a function of time, leads to an interrelation between these variables. Therefore the shape of the affinitively transformed nonisothermal kinetic curve (coordinates "transformation degree–time") will be determined, not only by the
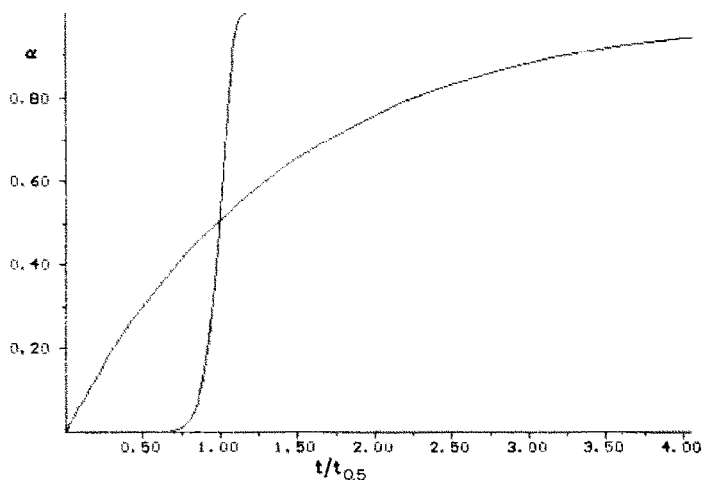
Fig. 1. Affinitively transformed isothermal and nonisothermal kinetic curves.

mechanism of the process, but also by the character of the temperature dependence of the rate constant. The impermissibility of affinitive transformation of the nonisothermal curve in the coordinates "transformation degree–time" was pointed out earlier [5]. Thus, the comparison of the shape of the affinitively transformed isothermal and nonisothermal curves made in Ref. 4 is invalid because of the fundamentally different information structure of the obtained curves, and cannot provide any information about the change in the mechanism of the process.

The foregoing is confirmed by Fig. 1, which shows the affinitively transformed (in accordance with Ref. 4) isothermal and nonisothermal curves corresponding to processes having the same mechanism (first-order reaction with the activation energy and preexponential values 125.4 kJ mol^{-1} and 10^{12} min^{-1}, respectively). It is seen from Fig. 1 that, notwithstanding the same mechanism of the process, the affinitively transformed isothermal and nonisothermal curves do not coincide. This example illustrates that the difference between the shapes of the above-mentioned curves is primarily a trivial result of the incorrect use of the affinitive transformation of the nonisothermal kinetic curve, rather than of the difference between the mechanisms of the corresponding processes.

Comparison of kinetic curves obtained under different experimental conditions, with the aim of elucidating the possible changes in the mechanism, can be made using the transformation of nonisothermal curves into an adequate isothermal form as proposed by us in Ref 6. This transformation permits reconstruction, at a given temperature, of the isothermal kinetic curve under the assumption that the mechanism of the process in isothermal and nonisothermal conditions is the same, which is formally manifested as the maintenance of the form of the process model at a change in the

experimental conditions. Proceeding from this assumption, we can write for the isothermal conditions

$$g(\alpha) = A_{ISO} \exp(-E_{ISO}/RT_{ISO})t \qquad (2)$$

and for the nonisothermal conditions

$$g(\alpha) = (A/\beta) \int_0^T \exp(-E/RT)\, \mathrm{d}T \qquad (3)$$

where $g(\alpha)$ is the integral form of the process model, β is the heating rate, t is time, A is the preexponential, and E is the activation energy. By virtue of the above assumption about the invariability of the mechanism of the process, we can equate the right-hand side of eqn. (2) with that of eqn. (3). Solving the obtained equality for time t, we obtain

$$t = A \int_0^T \exp(-E/RT)\, \mathrm{d}T \Big/ \big[\beta A_{ISO} \exp(-E_{ISO}/RT_{ISO}) \qquad (4)$$

The value of t obtained by this formula for the isothermal kinetic curve at a given temperature T_{ISO} corresponds to the transformation degree α complying with the temperature T on the nonisothermal curve at the heating rate β. Using eqn. (4), we can easily transform the nonisothermal kinetic curve into an adequate isothermal form. In turn, comparison of affinitively transformed kinetic curves, both those obtained in an isothermal experiment and those resulting from applying eqn. (4) to nonisothermal data, will make it possible to determine the possible change in the mechanism of the process caused by a change in the experimental conditions. Since the solution of this problem requires an affinitively transformed kinetic curve, we can use instead of the real time t the quantity t^* proportional to it. Proceeding from this, eqn. (4) can be considerably simplified

$$t^* = \int_0^T \exp(-E/RT)\, \mathrm{d}T \qquad (5)$$

In calculations, the temperature integral is replaced by the Senum–Yang approximation [7].

Let us test the proposed method of comparing kinetic curves on the above model data. The affinitively transformed isothermal curve and the nonisothermal one reduced by eqn. (5) to the isothermal form are given in Fig. 2. The coincidence of the kinetic curves points to the common mechanism of the process proceeding under isothermal and nonisothermal conditions, and thus confirms the adequacy of the method used.

Special attention should be paid to the fact that the efficiency of the proposed method is directly associated with the reliability of determining the activation energy of the process from nonisothermal data [see eqn. (5)]. The investigation made by us has shown that, in the general case, reliable values of the kinetic parameters can be obtained only by methods which do not use in calculations the discrimination of the mathematical models of the mecha-
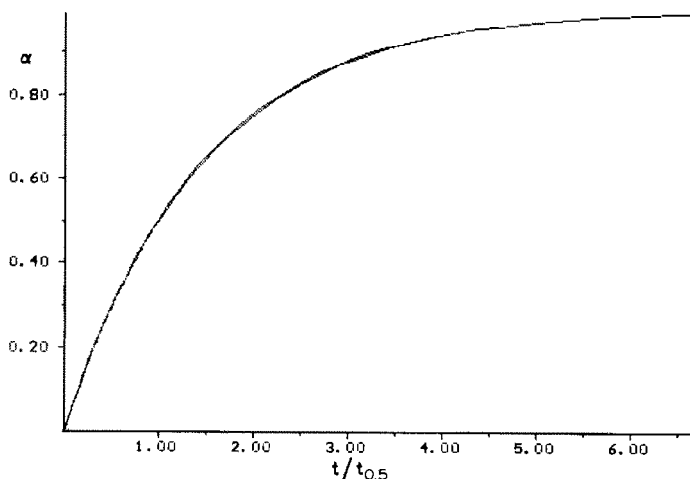
Fig. 2. Affinitively transformed isothermal kinetic curve and nonisothermal curve reduced to the isothermal form.

nism of the process. Among these are, for example, the isoconversion methods [8–10], which permit calculation of the values of the kinetic parameters by several nonisothermal kinetic curves for different transformation degrees. In this respect, similar to these methods are the quasi-isoconversion [11] methods [12–14] by which the kinetic parameters can be assessed by one kinetic curve. Just such methods are the most suitable for calculating the activation energy required for use of the transformation (4) proposed by us.

As to the above-mentioned methods, note that the quasi-isoconversion methods should be used [11] mainly to calculate the activation energy of gross single-stage processes. In the case of complex processes, we recommend [15] calculation of the effective activation energy by the isoconversion methods. A reliable criterion of the complex character of a process is [15] the existence of dependence of the activation energy, calculated by the isoconversion method, on the transformation degree. In calculating this dependence, the quasi-isoconversion methods prove to have limited efficiency. In the cases where the above criterion points to the complex character of the process, to calculate the values of t by eqn. (4) one should use the activation energy value corresponding to the transformation degree for which t is being calculated.

Obviously, the comparison of isothermal and nonisothermal kinetic curves which uses eqn. (5) is not applicable to all complex processes. The scope of its use is limited to processes whose kinetics can be described by the equation with separable variables

$$d\alpha/dt = k_{ef}(T) \cdot f_{ef}(\alpha) \qquad (6)$$

The rate constant and/or the process model have the meaning of effective characteristics. Among such processes are, for example, the complex process

[15] including two competing reactions having the same mechanism. The effective rate constant of such a process is equal to the sum of the rate constants of the competing reactions.

Thus, the inconsistency of isothermal and nonisothermal kinetic curves transformed by eqn. (5) in the case of a complex process can mean both a change in its mechanism caused by a change in the experimental conditions and the inapplicability of eqn. (6) for describing its kinetics. Therefore, to avoid ambiguous results for complex processes we recommend the use of eqn. (4) and compare affinitively transformed curves at the same temperature.

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