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An approach to the solution of the inverse kinetic problem in the case of complex processes.
Part III. Parallel independent reactions

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Abstract

This paper is devoted to the investigation of the possibility of identifying a complex process incorporating parallel independent reactions. The identification was achieved using a previously proposed method relying on the investigation of the form of the transformation-degree dependence of the effective activation energy. Using model data, we consider three main variants of the complex process and have established the characteristic dependences of their activation energy on the transformation degree. It is shown that the shape of these dependences is determined by the ratio of the rates of individual reactions and their partial contribution to the gross transformation degree and can be used for identifying the complex process under consideration.

INTRODUCTION

The authors of refs. 1 and 2 propose methods for calculating the Arrhenius parameters (AP) for complex processes incorporating parallel independent reactions. Obviously, the application of these methods requires reliable information on both the complex character of the process and its type (e.g. parallel independent reactions). In most cases, however, a priori information about the mechanism of the process is absent, and the only thing left to the researcher are the thermoanalytical curves by whose shape it is impossible to establish with any certainty the type of the process or, therefore, the form of the kinetic equation by which the AP values should be calculated. For example, in the case of an elementary (overall single-stage) and a complex process incorporating parallel competing or independent reactions (the results are given below), the thermoanalytical curves can have similar bell shape, although the kinetic equations for these processes are different. Thus, the identification of the type of complex process and the form of its corresponding kinetic equation is the first and, therefore, most important step in solving inverse problems because the correct choice of kinetic equation determines the reliability of the AP values that it calculates.

In the first paper [3] of this series, we proposed a method for identifying the type of complex process which relies on the analysis of the shape of the transformation-degree dependence of the activation energy calculated by the isoconversion method. As an example, in ref. 3 a complex process consisting of two parallel competing reactions was considered and it was found that such types of processes are characterized by an increasing dependence of the effective activation energy on the transformation degree. Extending the proposed method to different complex processes, we hope to create a sufficiently universal algorithm for identifying their types. The aim of the present paper is to study the possibilities of identifying a complex process incorporating parallel independent reactions by the proposed method.

MODELLING OF KINETIC CURVES

Let us consider an elementary model process incorporating two independent first-order reactions whose kinetics is described by the system of equations

$$\begin{aligned}(\mathrm{d}w/\mathrm{d}T)_1 &= k_1(1-w_1)/q \\ (\mathrm{d}w/\mathrm{d}T)_2 &= k_2(1-w_2)/q\end{aligned} \tag{1}$$

where w is the transformation degree, T is the temperature, k is the rate constant and q is the heating rate. Obviously, the ratio of k_1 and k_2 in a particular temperature range will determine the sequence of the corresponding reactions forming the complex process. In particular, these reactions can be time-separated. Because in this case the complex process degenerates into two elementary processes, it is of no special interest for us. We shall focus on the processes proceeding in parallel, i.e. simultaneously in the same temperature range.

Integrating the system of eqns. (1), we obtain a similar system of temperature dependences of the transformation degree

$$\begin{aligned}w_1 &= 1-\exp\left(-(1/q)\int k_1\,\mathrm{d}T\right) \\ w_2 &= 1-\exp\left(-(1/q)\int k_2\,\mathrm{d}T\right)\end{aligned} \tag{2}$$

Taking into account the Arrhenius shape of the temperature dependence of the rate constant $k=A\exp(-E/RT)$, we can easily calculate the integral in the Senum–Yang approximation [4]. The system of eqns. (2) contains the values of the partial transformation degrees, each of which is associated with a definite reaction. However, in the absolute majority of thermoanalytical experiments, a change in the gross physical quantities (mass, enthalpy, volume, etc.) is observed and, therefore, the partial transformation degrees for individual reactions are unknown. In this case, the gross transformation degree is the sum of the partial quantities

$$w = cw_1 + (1 - c)w_2 \qquad (3)$$

where c reflects the contribution of the first reaction to the change in the overall transformation degree. In the examples below we assume equal contributions of both reactions to the gross transformation degree, i.e. $c = 0.5$.

RESULTS OF THE CALCULATIONS

Let us consider three variants of the complex process incorporating two parallel independent reactions. In the first variant, the maximum on the differential kinetic curve for the reaction with the lower activation energy occurs at lower temperatures than that for the reaction with the higher activation energy. In the second variant the opposite is true. In the third variant the maxima are in the same temperature range. The transformation-degree dependences required for identifying the type of complex process have been calculated by one of the isoconversion methods [5] by the series of non-isothermal kinetics curves modelled according to eqns. (1)–(3) for four heating rates (1, 2, 4, 8°C min^{-1}).

Variant 1

The temperature of the differential thermoanalytical curve maximum for the reaction with the lower activation energy is lower than the corresponding temperature for the reaction with the higher activation energy. Such a variant of the process is observed, for example, for the following AP values of parallel reactions: $E_1 = 30$ kcal mol^{-1}, $A_1 = 10^{14}$ min^{-1}; $E_2 = 40$ kcal mol^{-1}, $A_2 = 10^{18}$ min^{-1}. Figure 1 shows the differential kinetic curves for this process. Analysing the shape of the obtained curves, it can be seen that they result from the superposition of two peaks and are likely to characterize a complex process incorporating two simultaneous reactions. This information can be obtained experimentally by thermoanalytical methods recording the change in physical quantities in differential form (DTA, DSC, DTG, etc.). Consequently, on the basis of experimental information we can make a suggestion about the type of complex process. However, as seen from Fig. 1, it is practically impossible to separate the processes (peaks). It is therefore impossible to obtain partial quantities of the transformation degree for individual reactions forming the process under study. As a result, the calculation of AP by eqns. (1) and (2) is not feasible.

To use the proposed method for identifying the type of complex process, it is sufficient to know the overall values of the transformation degree, the

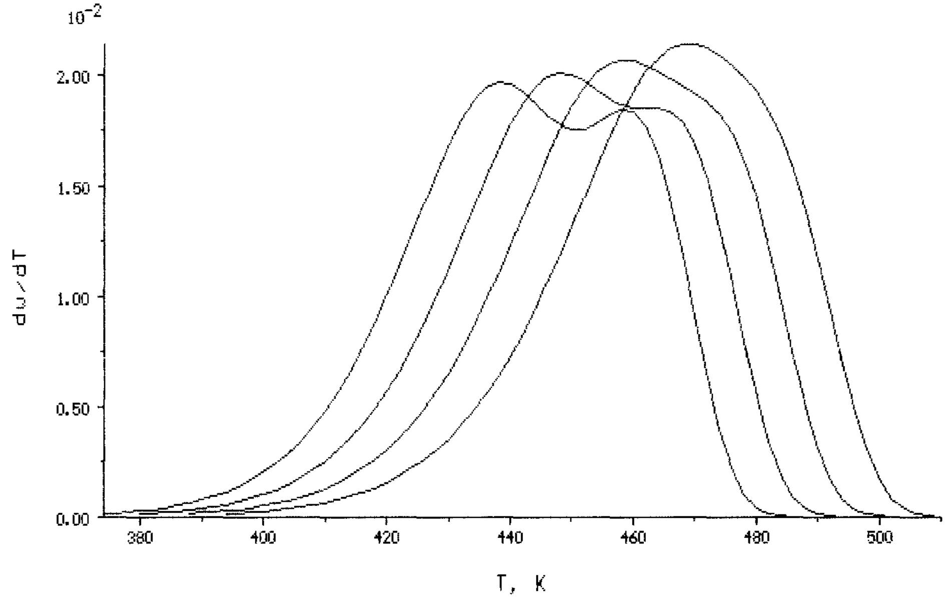

Fig. 1. DSC curves for the complex model process (variant 1).

calculation of which is not associated with any fundamental difficulties. Figure 2 shows the transformation-degree dependence of the effective activation energy calculated by the isoconversion method. This dependence

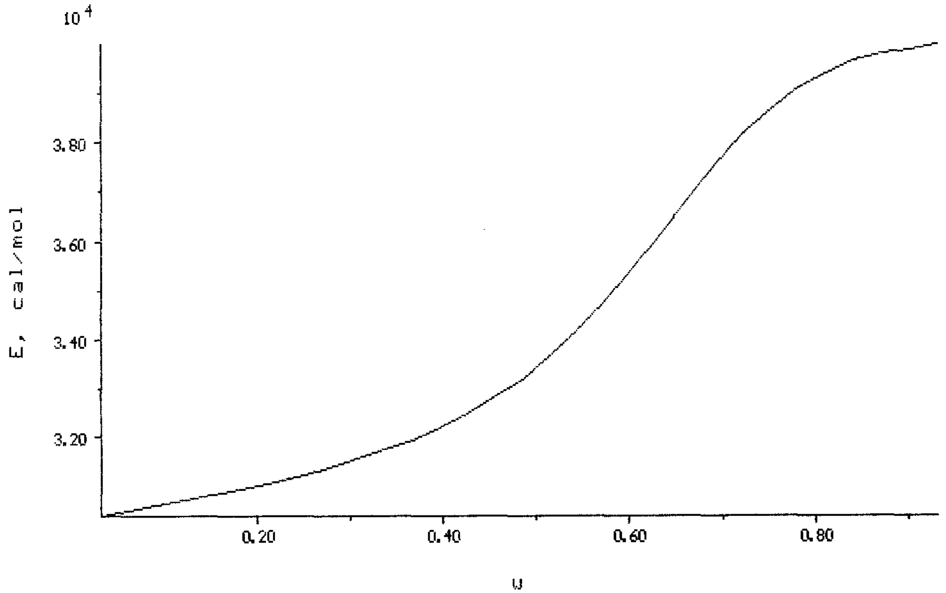

Fig. 2. Effective activation energy calculated by the isoconversion method vs. the transformation degree for the model process (variant 1).

increases with the range of transformation degree. The effective value of the activation energy extrapolated to zero degree of transformation (30.7 kcal mol^{-1}) is the estimate of the activation energy of the reaction prevailing at the initial stage of the transformation. Likewise, we can estimate the activation energy of the reaction prevailing at the final stage of transformation, assuming as the estimate the effective activation energy corresponding to the transformation degree of unity, i.e. 39.7 kcal mol^{-1}. The obtained values are fairly good estimates for true (model) values of activation energies of individual reactions. The slightly higher calculated value compared to the model values for the reaction with the lower activation energy is due to the fact that even at the initial stage, this reaction contributes materially to the gross transformation degree. In other words, for the given process, in the region of small transformation degrees the partial transformation degrees are comparable, although they are considerably different. In this connection, attention should be paid to the increasing nature of the dependence (Fig. 2) at transformation degrees close to zero, whereas in the region of transformation degrees close to unity, a plateau is observed. The absence of the transformation-degree dependence of the activation energy (plateau) points to the overall single-stage character of the process being investigated. Therefore, the presence of a plateau in the region of transformation degrees close to zero or 1 in dependences of the type given in Fig. 2 indicates that the calculated value of the activation energy corresponds to the overall single-stage process, i.e. it is actually the estimate of the activation energy of an individual reaction forming the complex process.

In the introduction, we noted that the increasing dependence of the effective activation energy on the transformation degree was established by us in ref. 3 for a complex process incorporating parallel competing reactions. However, there are two facts which make it possible to distinguish this process from that incorporating parallel independent reactions one of which (with a lower activation energy) prevails at the initial stage. Firstly, the increasing transformation-degree dependence of the activation energy in the case of the competing reactions, has no S-shape characteristic of the above process (Fig. 2). Secondly, the differential kinetic curves for the process incorporating competing reactions for all heating rates represent one peak, from the shape of which it is impossible to make any suggestions about the complex character of the process. Thus, analysing the shape of the differential kinetic curve and the transformation-degree dependence of the activation energy, we can distinguish complex processes incorporating parallel competing and independent reactions.

Variant 2

The temperature of the differential thermoanalytical curve maximum for the reaction with the lower activation energy is higher than the correspond-

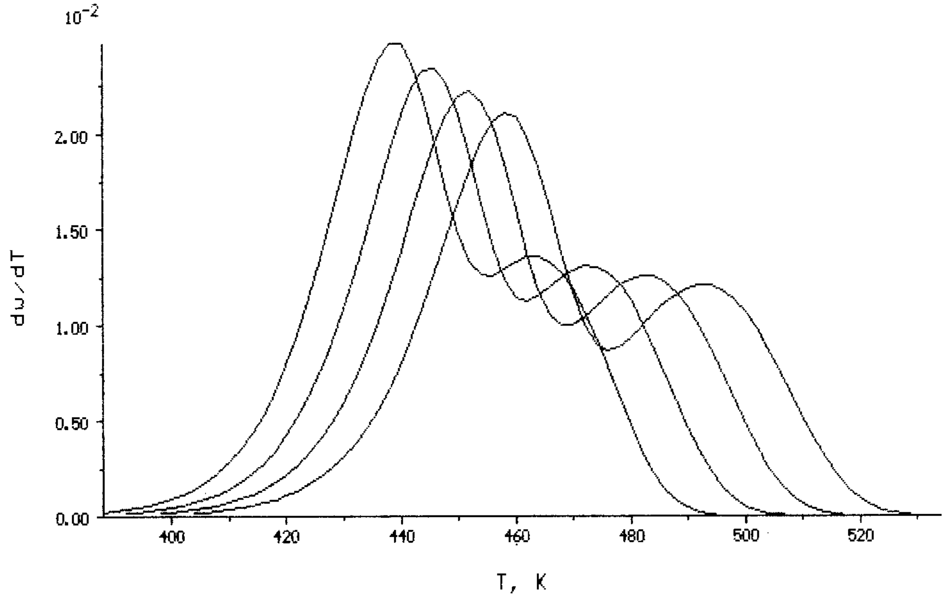

Fig. 3. DSC curves for the complex model process (variant 2).

ing temperature for reactions with the higher activation energy. Such a variant of the process is observed for the following AP values of individual reactions: $E_1 = 30$ kcal mol^{-1}, $A_1 = 10^{13}$ min^{-1}; $E_2 = 40$ kcal mol^{-1}, $A_2 = 10^{19}$ min^{-1}. The corresponding thermoanalytical curves are given in Fig. 3. As in the previous case, proceeding from the shapes of the thermoanalytical curves, we can describe the complex character of the process and make a suggestion about its type, but it is impossible to estimate the AP values of individual reactions from eqns. (1) and (2).

Let us consider information obtained by the proposed method of identifying the type of complex processes. The dependence of the effective activation energy on the gross transformation degree in the initial portion ($w = 0$–0.23) is increasing (Fig. 4). The portion of increasing effective activation energy is characteristic of the variant of the process under consideration because the reaction with the higher activation energy prevails at the initial stage and a rise in temperature causes a greater increase in the transformation degree as compared to the second reaction. Consequently, the increase in the effective activation energy reflects the growth of the partial contribution of the reaction with the higher activation energy to the gross transformation degree. Obviously, the effective value of the activation energy corresponding to the maximum partial contribution of the reaction with the higher activation energy to the gross transformation degree (in this case at $w = 0.23$) is the lower boundary of the estimate of the higher activation energy, 38.2 kcal mol^{-1}. The deviation of the obtained

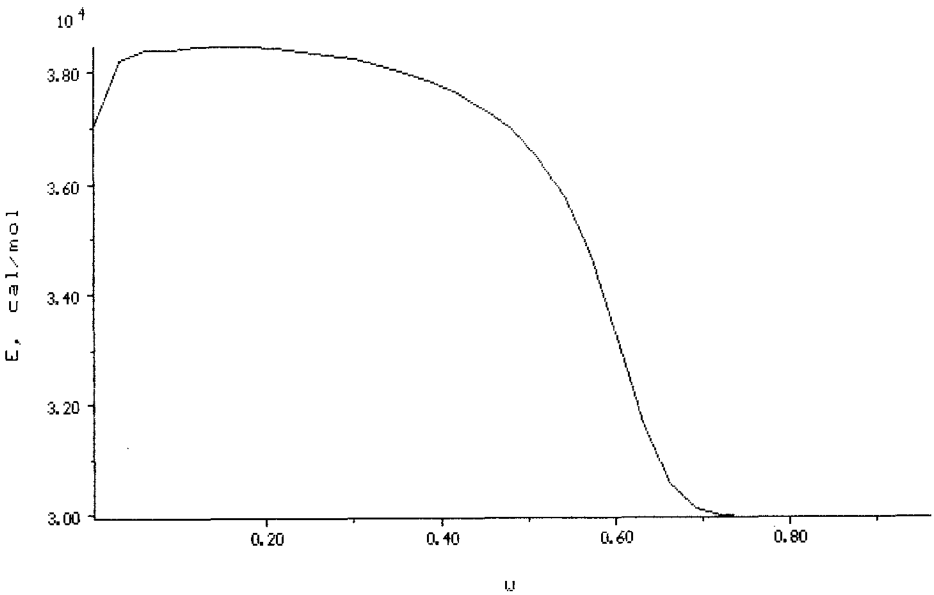

Fig. 4. Effective activation energy calculated by the isoconversion method vs. the transformation degree for the model process (variant 2).

estimate from the true value is small (less than 5%) which is quite satisfactory.

The decrease in the effective activation energy in the range of transformation degrees of 0.23–0.72 is associated with the growth of the partial contribution of the reaction with the lower activation energy to the gross transformation degree. In the above-mentioned range of transformation degrees, there is a gradual retardation of the reaction with the higher activation energy. The retardation, in the end, determines the kinetics of the overall process after the gross transformation degree of 0.23 is reached.

For transformation degrees higher than 0.72 on the transformation-degree dependence of the effective activation energy, a plateau is observed. In this region, the reaction with the higher activation energy is practically absent. Its rate at the gross transformation degree of 0.72 is lower by a factor of about 10^5 than that of the reaction with the lower activation energy. The maximum rate of the reaction with the lower activation energy is reached at the transformation degree of 0.81. So, in the 0.72–1.00 range of transformation degrees, the kinetics of the complex process is practically fully determined by the reaction with the lower activation energy, i.e. the process under consideration is an overall single-stage one. This fact is demonstrated by the presence of a plateau on the transformation-degree dependence of the activation energy (Fig. 4). The value of the effective activation energy close to 1 is a very good estimate of the lower activation energy of the reaction 30.0 kcal mol^{-1}.

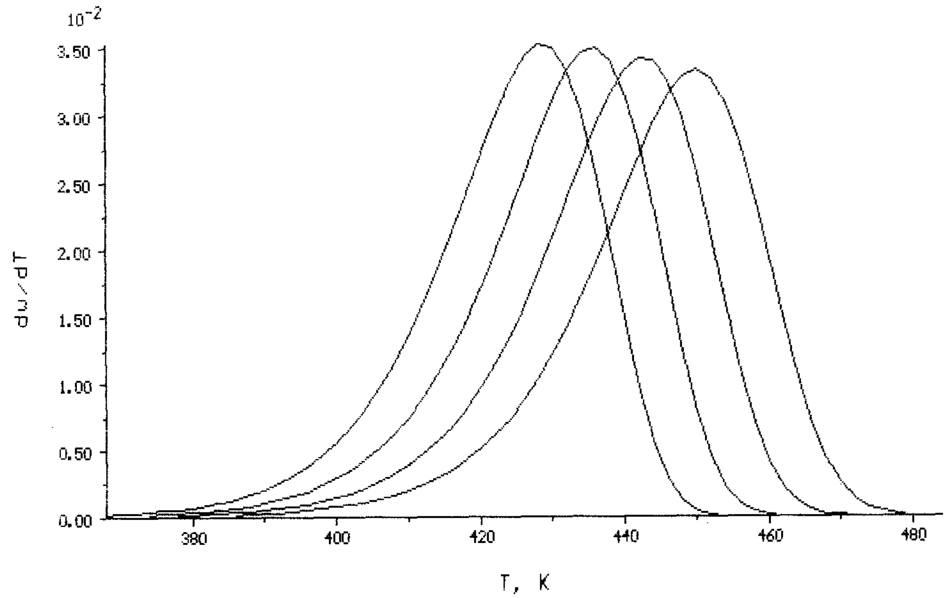

Fig. 5. DSC curves for the complex model process (variant 3).

Variant 3

The temperatures of the differential thermoanalytical curve maxima for both reactions practically coincide (maximum difference no greater than 5°C). Such a variant of the proceeding of the process is observed for the following AP values of individual reactions: $E_1 = 30$ kcal mol^{-1}, $A_1 = 2.2 \times 10^{14}$ min^{-1}; $E_2 = 40$ kcal mol^{-1}, $A_2 = 2.1 \times 10^{19}$ min^{-1}. In this case, unlike variants 1 and 2, the differential thermoanalytical curves (Fig. 5) are bell-shaped. Obviously, the ordinary shape of the thermoanalytical curves gives no reason for supposing that the process under study is complex. The standard procedure for calculation using the kinetic equation of the overall single-stage process

$$dw/dT = A[\exp(-E/RT)]f(w)/q$$

where $f(w) = (1-w)^n$, gives AP values intermediate between the true values (Table 1). Thus, both the calculated AP values and the shapes of the thermoanalytical curves in no way indicate the complex process of the process under study. Thus the obtained kinetic information describing the complex process as simple has no physical meaning.

Now, using our method of investigation, let us analyse the transformation-degree dependence of the effective activation energy (Fig. 6). First of all the very fact of the existence of such a dependence points unambiguously [3] to the complex nature of the process (for an elementary process the activation energy is constant for all transformation degrees). In addi-

TABLE 1

The results of calculating the kinetic parameters for the complex process (variant 3)

Heating rate (°C min^{-1})	Activation energy (kcal mol^{-1})	Pre-exponent (log min^{-1})	Reaction order
1	31.9	15.2	0.93
2	32.5	15.5	0.95
4	33.1	15.9	0.98
8	33.7	16.2	1.02

tion, the observable dependence reflects the kinetic laws of individual reactions forming the complex process. Thus, at small transformation degrees (0.1%) the partial contribution of the reaction with the higher activation energy is no greater than 12% of the gross value. Therefore, the value of the effective activation energy at small transformation degrees approximately corresponds to the reaction with the lower activation energy. For large transformation degrees (99%), both reactions make practically equal contributions to the gross transformation degree, as a result of which the quantity of the effective activation energy has a value close to the average activation energies of both reactions. The increasing portion of the dependence (Fig. 6) characterizes a more rapid increase in the partial contribution of the reaction with the higher activation energy to the gross transformation degree. The maximum on this dependence is in the middle

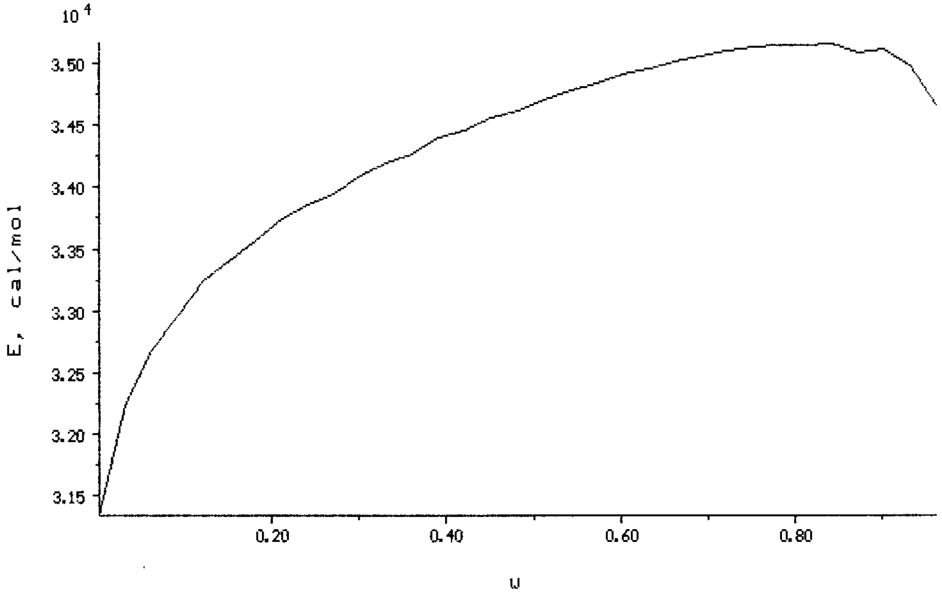

Fig. 6. Effective activation energy calculated by the isoconversion method vs. the transformation degree for the model process (variant 3).

of the range of transformation degrees (0.62–0.97) in which the maximum partial contribution of the reaction with the higher activation energy to the gross rate of the process at different heating rates is observed. The maximum value of the effective activation energy is an estimate of the higher activation energy. The relative error of such an estimate is 12%. The subsequent decrease in the partial contribution of the reaction with the higher activation energy to the gross rate of the process is accompanied by a decrease in the relative contribution of this reaction to the gross transformation degree, which causes a decrease in the effective activation energy of the process observed for high gross transformation degrees.

Thus, we have considered three main variants of the proceeding of a complex process incorporating two parallel independent first-order reactions and have found the corresponding dependences of the effective activation energy on the gross transformation degree. It is shown that the shape of a given dependence is determined by the ratio of the rates of individual reactions and their partial contribution to the gross transformation degree. However, because we have only considered the simplest variants of the process, the question arises quite naturally about the possibility of extrapolating the established types of dependences to the cases where the complex process incorporates more than two reactions or where individual reactions have an order other than unity. Taking into account the results of refs. 6–8, it may be supposed that the above-mentioned factors produce no decisive effect on the transformation-degree dependence of activation energy. Thus, practically all the dependences given in refs. 6–8 can be reduced to the three dependences found by us. Consequently, the above-mentioned dependences are characteristic of a complex process incorporating various independent reactions and can be used for its identification. Nevertheless, we deem it inexpedient to confine identification of the type of a real complex process to analysis of the shape of the transformation-degree dependence of activation energy. For example, it was noted above that the dependences increase for a complex process incorporating both parallel independent (variant 1) and competing reactions. Despite the fact that these dependences have different shapes, they can turn out to be indistinguishable in analysing real processes against the background of inevitable experimental error in calculating the effective activation energy. Therefore, in identifying the types of real processes, the results of analysing the shape of the transformation-degree dependence of activation energy should be supported by additional information.

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