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AN APPROACH TO THE SOLUTION OF THE INVERSE KINETIC PROBLEM IN THE CASE OF COMPLEX PROCESSES.
PART 1. METHODS EMPLOYING A SERIES OF THERMOANALYTICAL CURVES

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ABSTRACT

An approach to the solution of the inverse kinetic problem in the case of complex processes is proposed. This approach is based on the analysis of the dependence of activation energy calculated by the isoconversion method on the transformation degree. The inter-relationship between the shape of this dependence and the type of process has been determined. An algorithm for identifying the type of complex process in the simplest case is proposed. The possibility of assessing the parameters of individual stages has been investigated. All the calculations have been made using the isoconversion method for several model thermoanalytical curves.

INTRODUCTION

Approaches to the study of complex processes (those whose kinetics cannot be described as an overall single-stage process, i.e. by a single rate constant) on the basis of data from non-isothermal kinetics have been insufficiently developed. Despite the efforts made to describe kinetically particular complex processes cited in the literature [1–3], there is only one work [4] in which the general approach to the analysis of different complex processes is suggested. Obviously, the development of general approaches, one version of which is suggested in our paper, is of great interest from the viewpoint of practical kinetic studies. Apart from expounding the suitability of this approach to the analysis of complex processes, the present paper also attempts to compare the efficiency of its realisation using various methods for calculating the kinetic parameters. The first part of this paper is devoted to those methods relying on several thermoanalytical curves. The second part deals with the methods employing a single curve.

The development of approaches to the solution of the inverse kinetic problem in the case of complex processes is inhibited, in our opinion, by the traditional use by the majority of researchers of the discrimination method-

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ology [5] which, as was shown in ref. 6, does not permit, in the general case, an adequate determination of the kinetic parameters, even of an overall single-stage process. Therefore, it seems to us that any approach to the analysis of both complex and simple (overall single-stage) processes must rely on the methods relating to complementary techniques [5], or, in other words, using generalised descriptions of the process instead of discriminating separate elementary models. Among such methods are the isoconversion [7] methods and the method of invariant kinetic parameters (IKP) [8] (these will be considered in the first part), as well as the Šesták–Berggren [9], Piloyan [10] and exponential multipliers [4] methods (these will be considered in the second part of the article).

THE CRITERIA OF A COMPLEX PROCESS

Before beginning the kinetic analysis of a complex process, one should obviously make sure that this process is really complex, i.e. a reliable criterion of complexity is required. Isothermal kinetics uses, as such a criterion, the non-linear shape of the Arrhenius dependence [11]. However, the data obtained in the non-isothermal regime feature a strong dependence [12] of the kinetic parameter values on the type of model employed for the process, and the non-linear character of the Arrhenius dependence can be a trivial consequence of poor discrimination of the model. We therefore think it more reliable to use, as such a criterion, the transformation-degree dependence of the activation energy calculated by the isoconversion method. It was previously shown by us [13] that the existence of this dependence is an indication of the complex character of a process. To make sure of the validity of our considerations, let us compare the efficiencies of using the two above-mentioned criteria (the dependence of activation energy on the transformation degree and the non-linearity of the Arrhenius dependence) in order to determine the complex character of a model process.

Let us consider a model process involving two parallel competitive first-order reactions with the following values of the kinetic parameters: $E_1 = 20$ kcal mol^{-1}, $A_1 = 10^{12}$ min^{-1}, $E_2 = 35$ kcal mol^{-1}, $A_2 = 10^{18}$ min^{-1} (E is the activation energy, A is the pre-exponential coefficient). The rate of such a process is determined by the equation

$$\mathrm{d}\alpha/\mathrm{d}t = \beta\,\mathrm{d}\alpha/\mathrm{d}T = (k_1 + k_2)(1 - \alpha) \tag{1}$$

where α is the transformation degree, t is the time, T is the temperature, β is the heating rate, and k_1 and k_2 are the rate constants of the parallel reactions. Integrating eqn. (1), we obtain the temperature dependence of the transformation degree

$$\alpha = 1 - \exp\left[-(1/\beta)\int_0^T (k_1 + k_2)\,\mathrm{d}T\right] \tag{2}$$

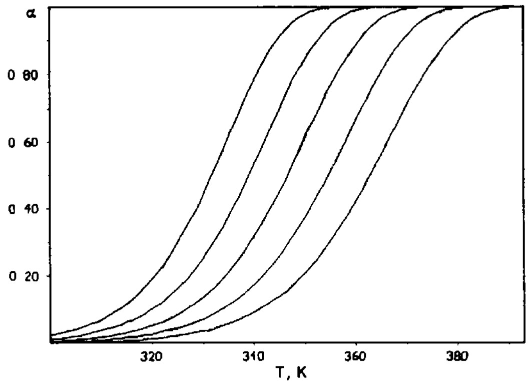
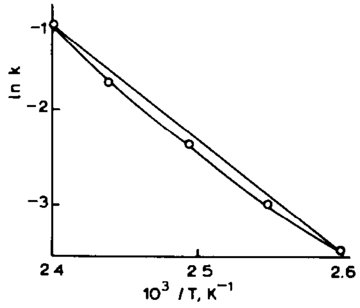


Fig. 1. The integral kinetic curves obtained for different heating rates (1, 2, 4, 8 and 16 °C min^{-1}) for the complex process involving two parallel reactions.

Taking into account the Arrhenius shape of the temperature-dependence of the rate constant, the integral can easily be calculated as a Senum–Yang approximation [14]. The integral kinetic curves obtained in this manner for different heating rates are given in Fig. 1.

Let us compare the results of calculations, using model data, by the IKP method and by the isoconversion method [15] which can be considered as a modification of the Ozawa method [16], taking into account the criticism contained in ref. 17. Figure 2 shows the dependence used in the IKP method of the logarithm of the isoparametric [18] rate constant on the inverse isoparametric temperature which, as was proved in ref. 19, is identical to the effective Arrhenius dependence. Analysing the latter (Fig. 2), we can notice (at least against the background of the straight line connecting the extreme points) that it is concave. As noted in ref. 11, such a dependence shape is characteristic of processes involving parallel competitive reactions. Thus, the



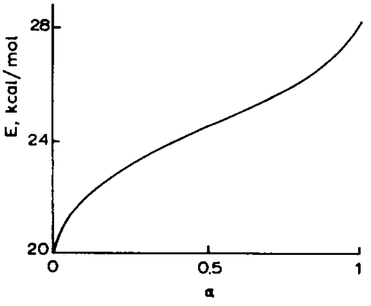


Fig. 2. The dependence of the logarithm of the isoparametric rate constant on the inverse isoparametric temperature for the complex process.

Fig. 3. The transformation-degree dependence of the effective activation energy calculated by the isoconversion method for the complex process.

type of the process being investigated can be identified by the shape of the Arrhenius dependence used in the IKP method. In practice, however, we would hardly be able to notice systematic deviations from linearity in the presence of deviations of experimental points on the Arrhenius dependence. As the result, some effective values of kinetic parameters have been calculated. In particular, the effective values of IKP in this case are: $E = 25.6 \pm 0.8$ kcal mol^{-1} and $\lg A = 12.8 \pm 0.5$.

Figure 3 shows the transformation-degree dependence of the activation energy effective value calculated by the isoconversion method. This dependence has a pronounced increasing character especially in comparison with the weak non-linearity of the Arrhenius dependence used in the IKP method. The high sensitivity of the transformation-degree dependence of the activation energy as against the Arrhenius dependence provides a higher efficiency of its application as a criterion of a complex process. The proposed approach to the analysis of complex processes is therefore based on the investigation of the transformation-degree dependence of the activation energy.

THE ALGORITHM FOR IDENTIFYING THE TYPE OF COMPLEX PROCESS

Let us assume, as a basis, the classification (proposed in ref. 11) of processes according to the type of non-linear Arrhenius dependences which are subdivided into convex and concave ones. As noted above, concave Arrhenius dependences (Fig. 2) are characteristic of processes involving several parallel reactions. The shape of the curve is, in this case, a natural consequence of the exponential (according to the Arrhenius law) temperature dependence of the reaction rate. As a result, as the temperature is increased, there is an increase in the partial contribution of the rate of a reaction with a higher activation energy to the value of the rate of the overall process. For this reason the effective value of the activation energy increases with increasing temperature and the Arrhenius dependence is concave. Taking into account the increasing character of the temperature dependence of the transformation degree and the relationship between the rate constant and the activation energy

$$\mathrm{d} \ln k/\mathrm{d}(1/T) = -E/R \tag{3}$$

we can determine the one-to-one relationship between the shapes of the transformation-degree dependence of the activation energy calculated by the isoconversion method and those of the non-linear Arrhenius dependence. The latter is readily found from the former by integration

$$\ln k = -\int E(\alpha)/R \, \mathrm{d}(1/T) + \text{const.} \tag{4}$$

By virtue of the established correspondence it is clear that concave Arrhenius dependences correspond to increasing and convex ones to decreasing transformation-degree dependences of activation energy.

An example of the processes leading to concave Arrhenius (Fig. 2) or increasing dependences of activation energy on the transformation-degree (Fig. 3) is the above-considered process involving parallel reactions. Similar dependences are given in ref. 1 for potassium permanganate thermolysis and in ref. 20 for coal pyrolysis.

The concave Arrhenius dependences (decreasing transformation-degree dependences of activation energy) are typical [11] of complex processes with a change in the limiting stage. Among these are, in particular, processes containing a reversible intermediate stage or those proceeding with a change-over from the kinetic to the diffusion regime.

The decreasing transformation-degree dependence of the activation energy was established by us [21] when analysing data on the kinetics of tetrazole thermolysis. This process proceeds through an intermediate reversible stage. We also observed decreasing dependences when studying the thermolysis of different woods and interpreted this fact as the transition of the process to the diffusion regime. It should be noted that the observed decreasing dependences had different shapes: concave in the presence of an intermediate reversible process and convex with the transition to the diffusion regime. The difference in the shapes of decreasing dependences, along with the additional information on the physico-chemical properties of the object of investigation, in this case can probably also be used in detailing the types of complex processes.

In the cited papers [1–3], the process of potassium oxalate monohydrate dehydration was investigated. In refs. 1 and 2, concave decreasing transformation-degree dependences of activation energy calculated by the isoconversion method are given, and ref. 22 presents the convex Arrhenius dependence as being typical of the oxalate dehydration process. It should be noted that while the authors of ref. 1 do not interpret this fact from the point-of-view of the mechanism of the process, in refs. 2 and 3 attempts are made to describe the process in question by the model of parallel reactions. Taking into account the above considerations, this model does not seem to be substantiated, because in the case of parallel processes the dependence of activation energy on the transformation degree must display an increasing character. Proceeding from the fact that the transformation-degree dependence of the activation energy [1,2] is decreasing and concave, we should most likely assume the presence of a reversible process, especially if we take into account that crystallohydrates, in general, undergo reversible dehydration, at least at the initial stage [23].

Therefore, we believe that on the basis of the investigation of the transformation-degree dependence of the activation energy calculated by the isoconversion method, we can substantiate a fairly universal approach to the

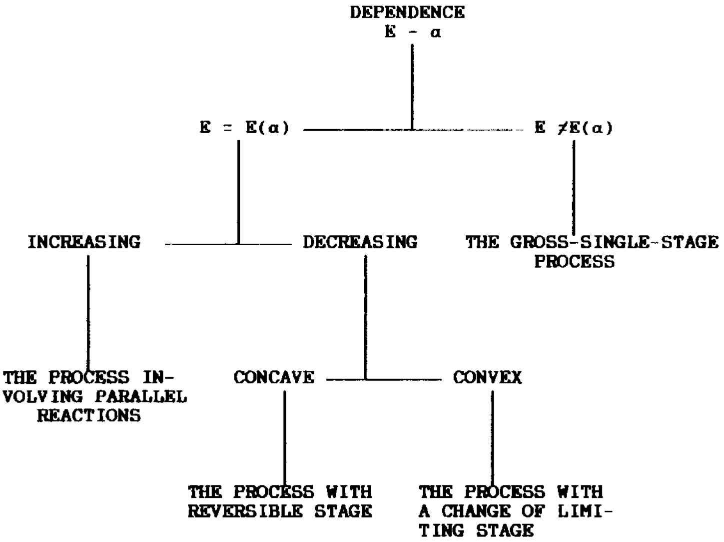


Fig. 4. The algorithm for solving the inverse kinetic problem for some typical cases of complex processes.

analysis of the kinetics of complex processes. The advantage of the proposed approach is the possibility of realising it as a simple algorithm (Fig. 4) which, of course, does not exhaust the whole diversity of complex processes, but only indicates the solution of the inverse kinetic problem in some most typical cases. Further investigation, using model data, of the relationship between the shape of the transformation-degree dependence of the activation energy and a particular type of complex process will obviously promote detailing of the above-mentioned algorithm and increase the efficiency of the proposed approach.

ESTIMATION OF THE KINETIC PARAMETERS OF INDIVIDUAL STAGES

Let us now compare the possibilities of estimating the values of the kinetic parameters of the reactions forming the complex process by the isoconversion and IKP methods using the example of processing data whose principle of modelling has been described above. According to the algorithm given in Fig. 4, the transformation-degree dependence of the activation energy calculated by the isoconversion method (Fig. 3) corresponds to the process involving parallel reactions. As the above dependence (Fig. 3) provides no information about the number of parallel reactions, it is felt that in this case we are dealing with a process consisting of at least two parallel reactions. As noted above, in the case of a complex process including parallel reactions, the partial contribution of the rate of a reaction with a higher activation energy to the overall rate of the process increases with increasing temperature–(transformation degree). Therefore, in order to estimate a lower activation energy the initial portion of the curve should be used and the estimation of a higher activation energy requires the use of the end portion. The value of the lower activation energy estimated in this way does not exceed 20.4 kcal mol^{-1} (transformation degree 1%) and that of the higher activation energy is no less than 27.8 kcal mol^{-1} (fractional conversion 99%). The validity of these estimates depends on the magnitude of a priori unknown partial contributions of individual reactions to the overall rate of the process at the beginning and end of the transformation, respectively. In our case the contribution of the reaction with the higher activation energy at the initial stage of transformation is immaterial, while the end of the conversion is characterised by a nearly equal contribution of each reaction. Therefore, one of these estimates is good and the other represents an intermediate value between the activation energy values of parallel processes.

The kinetic parameters of parallel reactions were also estimated by the IKP method. Calculation was made for the initial and end portions of the kinetic curve within the ranges of transformation degree from 0.01 to 0.05 and from 0.8 to 0.99, respectively. These portions differ in width, but they contain an equal number of points (about 20) because in modelling the data the temperature was varied in constant steps. As a result, the estimates of the kinetic parameters for the reaction with the lower activation energy are: $E_1 = 21.9 \pm 0.6$ kcal mol^{-1} and $\lg A_1 = 10.8 \pm 0.3$. For the reaction that proceeds with a higher activation energy the obtained values are: $E_2 = 26.0 \pm 0.7$ kcal mol^{-1} and $\lg A_2 = 12.7 \pm 0.4$. Comparing the values obtained by the IKP method with those calculated by the isoconversion method, it should be noted that the first method permits the estimation of both kinetic parameters, but the values of activation energy obtained by this method are somewhat worse than those obtained by the second method. However, the relationship between the quality of the activation energy estimates for parallel reactions is in this case the same as in calculations by the isoconversion method. It can therefore be stated that the accuracy of estimates of the kinetic parameters only slightly depends on the type of calculation method and is primarily associated with the information structure of the kinetic curve. If the contribution of the reaction to the overall rate of the process is small, the portion of information concerning it in the total volume of information obtained from the kinetic curve is also small. In turn, the shortage of information concerning an individual reaction leads to a limited possibility in determining its kinetic parameters.

CONCLUSION

The principal result of this study is the establishment of the relationship between the type of process and the shape of the transformation-degree dependence of the activation energy calculated by the isoconversion method, which permitted us to propose a general approach to the analysis of complex processes of various types. The described algorithm for identifying the types of particular complex processes vividly demonstrates the efficiency of the proposed approach in solving the inverse kinetic problem. It should be noted that the accuracy of estimating the kinetic parameters of individual stages is directly associated with the information structure of the kinetic curve and can be low. However, the approximate values of the kinetic parameters associated with the real stages of the process in question are far more valuable than the "exact" values of the kinetic parameters of a complex process obtained assuming that it is an overall single-stage process. We therefore believe that to avoid the calculation of "exact" but meaningless values of the kinetic parameters, it is necessary to investigate the transformation-degree dependences of the activation energy estimated by any isoconversion method prior to calculating the parameters by any method.

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