

An approach to the solution of the inverse kinetic problem in the case of complex processes.

Part 4. Chemical reaction complicated by diffusion

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Abstract

The complex process comprising chemical reaction and diffusion is analysed by means of the previously proposed approach. It is suggested that such processes be considered as the consecutive reactions representing the formation of the surface layer and the diffusion of gaseous products through it. Using both the model and experimental data, it is shown that the proposed approach identifies the hypothetical scheme of the process, reveals the limits of its proceeding in a kinetic or diffusion regime, and estimates their kinetic parameters.

INTRODUCTION

The overall rate of a heterogeneous process is generally defined by the rates of chemical reaction and diffusion [1–5]. It is known [1] that most processes proceed in a mixed regime in which the rates of chemical reaction and diffusion are comparable. Thus the necessity of taking into account the diffusion when studying the kinetics and mechanism of a heterogeneous process is obvious. Classical kinetics [6] solves this problem by inserting the diffusion rate into the kinetic equation; thus, in the case of one-dimensional diffusion, the kinetic equation becomes

$$\partial c / \partial t = D \partial^2 c / \partial x^2 - kf(c)$$

However, the practical application of this equation is not possible without a knowledge of the reagent distribution in the reaction area. Nevertheless, thermal analysis methods widely employed in studying the processes of heterogeneous thermolysis give no such information. Experimental methods of isolating the chemical stage [1, 2] could provide a solution to some extent, but they are highly sophisticated and are only developed for isothermal conditions. Therefore, in practice, kinetic processing of thermal analysis data comprising information from a mixed regime becomes problematic.

The intent of this work is to offer a simple way of solving the above problem with the help of a previously proposed approach [7] from the analysis of the kinetics of complex processes. This approach is based on the isoconversional calculation of the Arrhenius parameters and requires some thermoanalytical experiments at different heating rates. Its efficiency was confirmed in identifying the mechanism of some real complex processes [8–12]. It is also pertinent to mention the KinTool software [13], which was developed on the basis of this approach for solving applied kinetic problems [14–16] connected with extrapolating substance behaviour beyond the experimental temperature region.

THEORY

From our viewpoint, the processes comprising a chemical reaction complicated by diffusion can be considered as a system of consecutive reactions $A \rightarrow P \rightarrow B$, where the intermediate P is the original substance A, covered by a layer of product B. Because the temperature dependences of chemical reaction and diffusion are described by the Arrhenius equation, $k = A \exp(-E/RT)$, with the respective constants k_1 and k_2 , three kinds of mixed process can be considered: $k_1 \gg k_2$; $k_1 \ll k_2$; $k_1 \approx k_2$.

In the first case, a chemical reaction instantly yields a surface layer of the product, diffusion through which limits the kinetics of the overall process. The second case is observed when the diffusion rate is much higher than the chemical reaction rate. As a result the surface layer has no influence on the process kinetics whose rate is determined by the chemical reaction alone. Both of these cases imply a process proceeding in either a totally kinetic or a totally diffusion regime. Thus, their more detailed analyses lie beyond the scope of this paper.

We have concentrated on the third case, in which the process takes place in a mixed regime. As an example, we have chosen a model process comprising a first-order chemical reaction (activation energy $E_1 = 40 \text{ kcal mol}^{-1}$ and pre-exponent $A_1 = 10^{26} \text{ min}^{-1}$) and a diffusion process ($E_2 = 4 \text{ kcal mol}^{-1}$ and pre-exponent $A_2 = 40 \text{ min}^{-1}$), obeying the Jander model [3, 4]. For this process, the temperature at which $k_1 = k_2$ is about 322 K. If we model the DSC curves so that this temperature is within the temperature range of the process, the overall process rate at onset temperature will be almost completely determined by the chemical reaction. As the temperature and surface layer of the product increase, the process will gradually turn into a diffusion regime.

For consecutive reactions the heat release is determined by the rates and thermal effects of the stages

$$I(T) = Q_1(-d[A]/dt) + Q_2(d[P]/dt)$$

Because in our case, both stages are the same process of transforming A

into B, but by different means (kinetic and diffusion), the thermal effects are equal. Let us assume that $Q_1 = Q_2 = 10 \text{ kcal mol}^{-1}$. The rates of consuming original substance and forming intermediate material for this process are described by the system of differential equations

$$-d[A]/dt = k_1(T)[A]$$

$$d[P]/dt = k_1(T)[A] - k_2(T)[P]^{2/3}/(1 - [P]^{1/3})$$

the solution of which was determined by the Runge–Kutta method [17] at the respective heating rates $q = dT/dt = 8, 12, 16 \text{ K min}^{-1}$. The initial conditions were set as $[A]_0 = 0.9999$ and $[P]_0 = 0.0001$. The onset temperature was defined as a solution of the first equation of the above system.

RESULTS AND DISCUSSION

The obtained DSC curves were placed in the temperature interval 300–420 K and have the expected bell-shaped form (see Fig. 1). Figure 2 shows the overall transformation degree dependence of the effective activation energy calculated by the isoconversional method for the process being studied. It should be noted that the shape of the observed dependence for such processes was predicted earlier [7] from theoretical considerations. Moreover, the decreasing transformation degree dependence of the activation energy corresponds to the convex Arrhenius dependence obtained theoretically by Zel'dovich [18] for processes proceeding in a mixed regime.

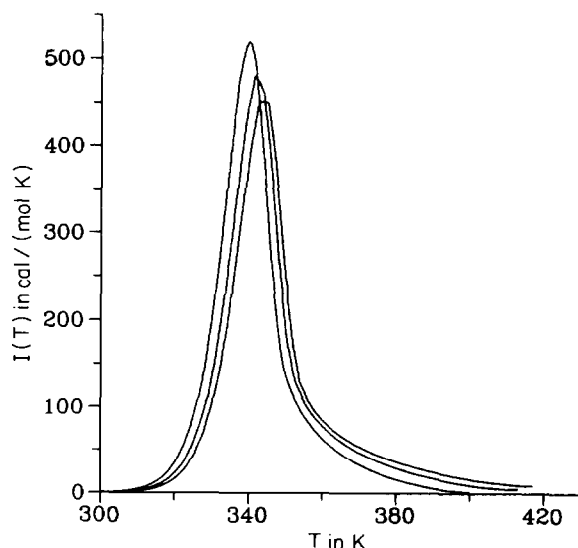


Fig. 1. The model DSC curves for the complex process of a chemical reaction complicated by diffusion at heating rates of 8, 12 and 16 K min^{-1} .

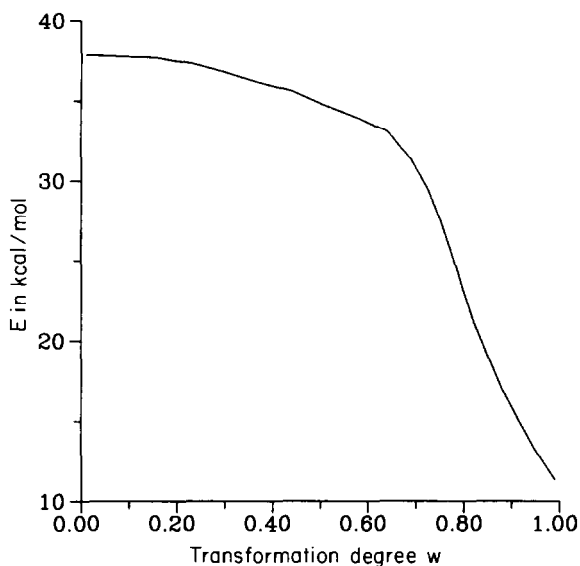


Fig. 2. The transformation degree dependence of the activation energy for the model complex process.

From the shape of the dependence presented in Fig. 2, one can conclude that the process under study is complex because the effective Arrhenius parameters of a simple (overall single-stage) process do not depend on the transformation degree. Consequently, the limiting stage of this process has changed. The low value of the activation energy at high transformation degrees is more characteristic of the solid-state diffusion of a gas than of solid-state thermolysis. Thus, a shift from a kinetic to a diffusion regime of thermolysis may be assumed.

Moreover, from the shape of the obtained dependence, the influence of diffusion at any stage of a process can be estimated. In particular, for the process under study we can say that up to a transformation degree of about 0.2, the process is almost completely single-stage and its rate is mostly determined by the chemical reaction. The slight influence of diffusion at this stage is apparent when the calculated activation energy is revealed to be slightly less than the model value for this process. But in a real situation, dealing with experimental data for which the true activation energy is unknown, the influence of diffusion would scarcely be detected. Thus we have to consider the above stage as a kinetic one. The practical value of this kind of information is that it reveals the area in which the process rate can be changed by chemical means. Obviously, in a diffusion regime, chemical means will produce no effect on the process rate.

Dependences similar to that shown in Fig. 2 were obtained after kinetic processing of experimental data from wood thermolysis [19] (Fig. 3). From the shapes of these dependences, we can conclude that the thermolysis of

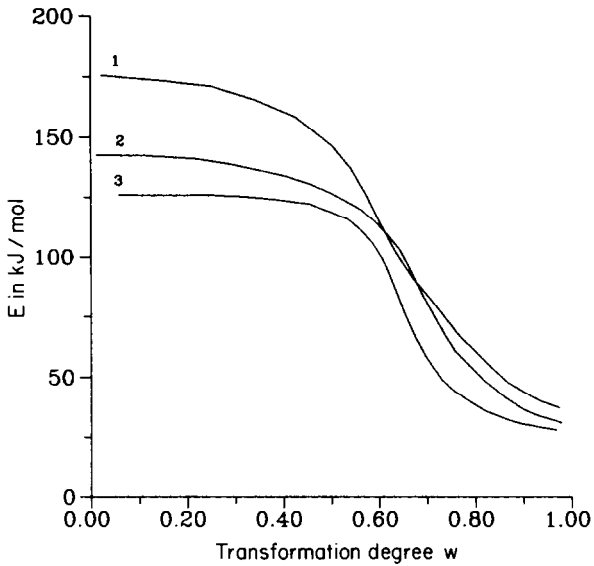


Fig. 3. The transformation degree dependences of the activation energy for the process of wood thermolysis: 1, pine; 2, birch; 3, oak.

wood proceeds with transition from kinetic to diffusion regimes. The activation energy values for the kinetic regime (up to a transformation degree of nearly 0.5) of thermolysis corresponds to values [20] calculated from data obtained from isothermal experiments carried out at temperatures less than 340°C. Moreover, as stated in this review article [20], increasing the temperature of the isothermal experiment leads to a decreasing in the activation energy of a process. To explain this effect, we will apply the model proposed here for the processes proceeding in the mixed regime. In accordance with the model, increasing the temperature accelerates the formation of the intermediate product P (original substance A covered by a layer of product B). It is this which transforms the process into a diffusion regime, which are characterized by low activation energies.

The dependences depicted in Fig. 3 allow the activation energy for diffusion of the products of wood thermolysis to be estimated as the value of the effective activation energy at a transformation degree of close to unity. This value corresponds to the activation energy of 49 kJ mol⁻¹ found in ref. 21 from the data of isothermal experiments carried out in the range 350–650°C.

CONCLUSIONS

Processes proceeding in a mixed regime can be analysed as consecutive reactions representing the formation of the surface layer and the diffusion of gaseous products through it. The previously proposed approach to the

analysis of complex reaction kinetics can be used to identify a hypothetical scheme for the process being studied, disclosing the limits of its proceeding in a kinetic or diffusion regime and estimating the kinetic parameters for them. Hence, this approach can be successfully employed for kinetic processing of thermal analysis data for processes consisting of chemical reactions complicated by diffusion.

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