APPLICATION OF THERMAL ANALYSIS TO THE STUDY OF THE KINETICS OF TWO-STAGE REACTIONS

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A method is suggested for studying the kinetic parameters of two-stage reactions from thermoanalytical experimental data. The method allows determination of the kinetic characteristics of the process on the basis of integral thermoanalytical data, without separation of the individual stages. Parallel, independent and successive reactions taking place under isothermal and non-isothermal conditions are considered.

The study of multistage reactions is one of the current problems of thermal analysis. The fundamental aspects of the problem have been discussed in [1, 2], where the utilization of multiparameter-programmed heating is suggested for study of the kinetics of multistage reactions. Another current approach for solution of the reverse-kinetics task, the determination of the reaction mechanism under given conditions from experimental data, consists in selecting the type of kinetic relationship by means of a computer [3, 4]. However, for practical thermoanalytical purposes it is above all important to develop relatively simple laboratory methods to identify the stages of the chemical reaction, to establish their type and to determine the effective kinetic constants. This paper deals with the development of a method for such purposes.

The simplest reactions are considered, viz. (i) parallel monomolecular reactions: $A \rightarrow B$, $A \rightarrow C$; (ii) simultaneously proceeding independent monomolecular reactions: $A \rightarrow B$, $C \rightarrow P$; (iii) two-stage successive reactions consisting of monomolecular stages: $A \rightarrow B \rightarrow C$.

Although this kinetic approach is formal, it should be noted that such reactions do occur in practice. This is the case, in particular, for all parallel, independent or successive reactions, where and hence its concentration remains practically unchanged during the reaction (oxidation, hydrogenation, chlorination, etc.).

The parameters to be determined are the frequency factors and activation energies for the individual stages: K_1, E_1, K_2 and E_2. The starting experimental

data depend on the thermoanalytical method applied. For DTA and differential scanning calorimetry considered in this paper, they are as follows: temperature T, momentary and final amounts of heat evolved (or absorbed) q and q_∞, and rate of heat evolution $\dot{q} = dq/dt$. The values $\ddot{q} = d^2q/dt^2$ and $\dot{T}$ (in non-isothermal experiments) are also obtained experimentally they are required in the following analysis.

First of all it is necessary to establish that the reaction actually does proceed in stages, since by varying the experimental conditions it is not always possible to separate the individual stages of the process. If the experimental data do not allow a direct conclusion as to the stages of the reaction, the following simple method is suggested. In the most general case, a one-stage reaction is described by the following equation: $\dot{q} = k \exp(-E/RT) f(q)$. If a series of experiments are performed at different heating rates or at different temperatures (isothermal experiment) and the isothermal section ($q_* = $ const) is drawn [1], a set of values ($\dot{q}_*$, T_*) corresponding to the given q_* value will be obtained. The number of pairs of values is equal to the number of experiments. For a one-stage reaction, linearization‧ will proceed in the coordinate system $\ln \dot{q}_*$ vs. $1/T_*$; absence of linearization indicates a multistage reaction.

The equations describing the heat evolution rates $\dot{q}$ for the above-listed two-stage reactions are as follows: for parallel reactions (A →B, A →C):

$$\dot{q} = \left[A_0 - \frac{q_1}{Q_1} - \frac{q_2}{Q_2} \right] \left[Q_1 K_1 e^{-E_1/RT} + Q_2 K_2 e^{-E_2/RT} \right] \tag{1}$$

for independent reactions (A →B, C →P):

$$\dot{q} = Q_1 K_1 e^{-E_1/RT} \left(A_0 - \frac{q_1}{Q_1} \right) + Q_2 K_2 e^{-E_2/RT} \left(C_0 - \frac{q_2}{Q_2} \right) \tag{2}$$

and for successive reactions (A →B →C):

$$\dot{q} = Q_1 K_1 e^{-E_1/RT} \left(A_0 - \frac{q_1}{Q_1} \right) + Q_2 K_2 e^{-E_2/RT} \left(\frac{q_1}{Q_1} - \frac{q_2}{Q_2} \right) \tag{3}$$

The amount of heat Q evolved or absorbed is described in general by the relationship

$$q = q_1 + q_2 \tag{4}$$

In the above equations, A_0 and C_0 are the initial molar concentrations of the starting materials: Q is the thermal effect of the reaction (cal/mol), and 1 and 2 are subscripts denoting the first and the second stage, respectively.

In this paper, a method will be described for determination of the kinetic parameters of these reactions from the thermoanalytical data under isothermal and non-isothermal conditions.

I. Isothermal experiment

Under isothermal conditions, $B_1 = K_1 \exp(-E_1/RT)$ and $B_2 = K_2 \exp(-E_2/RT)$ are constant values.

Parallel reactions

It follows from Eq. (1) that $\dot{q}_1 = Q_1 B_1 q/(Q_1 B_1 + Q_2 B_2)$ and $\dot{q}_2 = Q_2 B_2 \dot{q}/(Q_1 B_1 + Q_2 B_2)$. If q_1 and q_2 are determined by integration and substituted into Eq. (1), the kinetic equation

$$\dot{q} = A_0(Q_1 B_1 + Q_2 B_2) - (B + B_2 q) \tag{5}$$

is obtained.

Then, for parallel two-stage reactions a linear function $\dot{q}(q)$ must exist. The slope of this straight line is $a = B_1 + B_2$, and the intercept on the $\dot{q}$ axis is $c = A_0(Q_1 B_1 + Q_2 B_2)$. If the values Q_1 and Q_2 are known, then, by determining a and c, one finds B_1 and B_2 from the conditions

$$B_1 = \frac{c - Q Q_2 A_0}{A_0(Q_1 - Q_2)}; \quad B_2 = a - B_1 \tag{6}$$

If a series of experiments are performed at various T values and $B_1(T)$ and $B_2(T)$ are determined the relationship $\ln B$ vs. $(1/T)$ can be established. The slope of the straight lines obtained will yield E_1/R and E_2/R, and the intercepts on the ordinate axis will yield $\ln k_1$ and $\ln k_2$, respectively.

If Q_1 and Q_2 are not known, their values can be found by constructing the relationship $Q_\infty(T)$, which in the ranges of low and high temperatures will tend asymptotically towards $A_0 Q_1$ and $A_q Q_2$, if the first reaction proceeds at high rates in the range of low temperatures and the second reaction does so in the range of high temperatures. Then, the mere existence of the relationship $q_\infty(T)$ is additional evidence that parallel reactions take place. If one cannot separate the reactions and determine Q_1 and Q_2 in this manner, their values can be calculated as follows: Three experiments are carried out at three temperatures T_i ($T_3 > T_2 > T_1$), and a_i and c_i are determined from Eq. (6). One can then readily obtain a transcendent equation, the roots of which will yield the values of Q_1 and Q_2:

$$p \ln \frac{c_2 - x a_2 A_0}{c_1 - x a_1 A_0} = d \ln \frac{c_1 - x a_1 A_0}{c_3 - x a_3 A_0} \tag{7}$$

where $d = (T_2 - T_1)/RT_1T_2$ and $p = (T_3 - T_1)/RT_1T_3$. Even if one of the reactions is thermally neutral, one can determine the parameters of both reactions, since a kinetic connection exists between the reactions by means of $\dot{q}$ and q from Eq. (5). The criterion of such a situation is the change of q_∞ when T is varied from some value to zero, or the vanishing of one of the roots of Eq. (7).

Independent reactions

In this case, independently of the experimental temperature, q_∞ is constant, and the experimentally determined value is $q_\infty = A_0Q_1 + C_0Q_2$. By expressing q_2 in Eq. (2) in terms of q and q_1 from Eq. (4) and taking its derivative with respect to time, one obtains

$$\frac{\ddot{q}}{q_\infty - q} = B_1B_2 - (B_1 + B_2)\frac{\dot{q}}{q_\infty - q} \tag{8}$$

Hence, the criterion for the occurrence of two independent monomolecular reactions is the existence of the linear relationship $\ddot{q}/(q_\infty - q)$ *vs.* $\dot{q}/(q_\infty - q)$. The slope of this straight line is $a = B_1 + B_2$, and the intercept on the ordinate is $c = B_1B_2$. In the knowledge of a and c, one can determine B_1 and B_2 from the condition

$$B_{1,2} = \frac{a}{2} \pm \sqrt{\frac{a^2}{4} - c} \tag{9}$$

By carrying out a series of experiments at different temperatures and constructing the relationship $\ln B_1$ and $\ln B_2$ *vs.* $1/T$, one can find the kinetic parameters of both reactions. As may be seen from Eq. (8), in this case it is not necessary to know Q_1 and Q_2 to be able to determine the kinetic constants; it is enough to determine the value of q_∞ experimentally. It should be noted, however, that if one of the reactions is thermally neutral, then (since there is no kinetic connection, but only a thermal connection between independently proceeding reactions) the experimental data will allow determination of the parameters only of that reaction which is accompanied by heat evolution (absorption).

Successive reactions

In the case of such reactions, it is necessary to identify the fact that successive reactions actually take place, to elucidate the scheme for determining the kinetic constants and to establish the order of succession. By substituting q_2 by q and q_1 and taking the second derivative of Eq. (3), one obtains an equation analogous to Eq. (8), where $q_\infty = A_0(Q_1 + Q_2)$. Thus, it is not necessary, for successive reactions either, to know the values of Q_1 and Q_2, but only the value of q_∞ in order to be able

to determine the kinetic constants. Consequently, linearization in the coordinates $\ddot{q}/(q_\infty - q)$ vs. $\dot{q}/(q_\infty - q)$ indicates that either independent of successive reactions take place. For independent reactions, however, the function $\dot{q}(t)$ decreases monotonously with time, whereas in the case of successive reactions its character is extremal. The fact that extrema exist, and consequently that successive reactions take place, can be established by varying the temperature of the isothermally performed experiments.

Determination of the kinetic parameters on the basis of the linear relationship $\ddot{q}/q_\infty - q$ vs. $\dot{q}/q_\infty - q$ for successive reactions is analogous to that described above for independent reactions. However, for independent reactions their order of succession is of no importance, whereas in the case of successive reactions it is indispensable to find out which B values determined via Eq. (9) relate to the first reaction and which to the second.

For this purpose, the extremal character of the kinetic curve for the intermediate can be utilized. According to [5], the concentration of the intermediate is maximum at the moment $t_0 = \dfrac{\ln B_2/B_1}{B_2 - B_1}$. Owing to the symmetry of this expression, the value t_0 is determined unequivocally, independently of B_i relating to the first or to the second reaction. At the moment t_0, $\dot{q} = q_\infty B_1 \exp(-B_1 t_0)$, and $\ddot{q} = -B_1^2 Q_1 A_0 \exp(-B_1 t_0)$. Consequently, $[\ddot{q} - q_\infty/\dot{q}]_{t=t_0} = -B_1 Q_1 = \alpha$. If two experiments are performed, at the temperatures T_1 and T_2, the α_1 and α_2 values are obtained, their ratio yielding B_1^1/B_2^2. Then, those B values whose ratio at T_1 and T_2 is equal to α_1/α_2 will correspond to the first reaction. From the value B_1 determined the condition $A_1 = \alpha/B_1$, and $Q_2 = (q_\infty - A_0 Q_1)/A_0$.

If the second reaction is thermally neutral, then (since it will not kinetically affect the first reaction) only the parameters of the first simple one-stage reaction will be determined in the experiment, and in this case the above-considered criterion of the one-stage reaction is applicable. On the other hand, if the first reaction is thermally neutral, then (since the second reaction is kinetically connected with the first reaction) the kinetic parameters of both reactions can be found by the above-considered scheme.

The suggested schemes for determining the kinetic parameters were checked in a computerized experiment. The initial parameters of the problem were $K_1 = 0.43 \cdot 10^4$ min^{-1}; $K_2 = 0.3 \cdot 10^{19}$ min^{-1}; $E_1 = 39.39$ kJ/mol; $E_2 = 167.6$ kJ/mol; $Q_1 = 419$ kJ/kg; and $Q_2 = 2095$ kJ/kg. The process temperatures were 400–460 K. Tme values q, $\dot{q}$ and $\ddot{q}$ were computed. Figure 1 presents the function $\dot{q}(q)$ for the case of parallel reactions. A linear relationship, as follows from Eq. (5), is observed. Figure 2 shows that, in the case of independent and successive reactions, linearization actually takes place in the coordinate system $\ddot{q}/(q_\infty - q)$ vs. $\dot{q}/(q_\infty - q)$. The parameters obtained with the above schemes were in good agreement
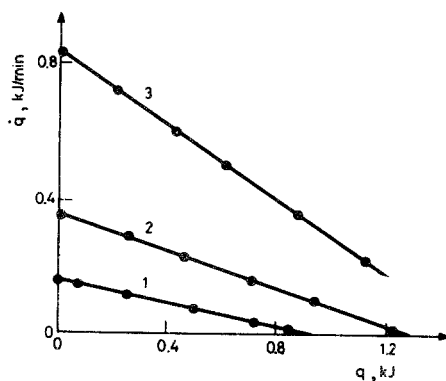
Fig. 1 Relationship $\dot{q}$ vs. q for parallel monomolecular reactions (1) 440 K; (2) 450 K; (3) 460 K
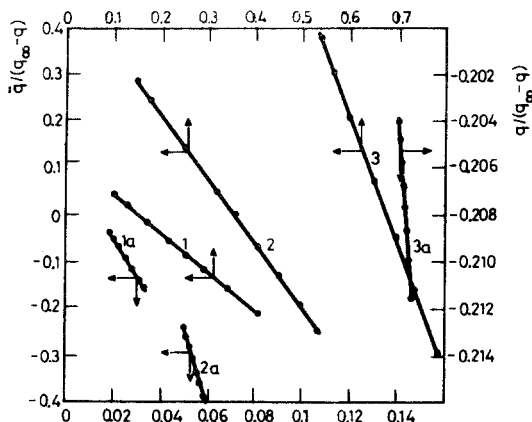

Fig. 2 Relationship $\ddot{q}/(q_\infty - q)$ vs. $\dot{q}/(q_\infty - q)$ for independent and successive reactions (a – independent reactions) (1) 430 K; (2) 440 K; (3) 450 K

with the initial data: the error in the activation energy was within 3%, and that in the frequency factor within 30%.

II. Non-isothermal experiment

Parallel reactions

When parallel reactions proceed under non-isothermal conditions, q_∞ will not remain constant, but will change with the heating rate w from $Q_1 A_0$ to $Q_2 A_0$. Such behaviour of q_∞ may serve as the criterion for parallel reactions taking place.

Through change of the heating rate w and construction of the relationship $q(w)$, the values of Q_1 and Q_2 con be obtained if they were unknown previously.

On substitution of Q_2 by q_1 and q in Eq. (1) and differentiation of this equation with respect to time, the following expression is obtained

$$\frac{\ddot{q}}{\dot{q}} = -(B_1 + B_2) + \frac{Q_1 B_1 B_3 + Q_2 B_2 B_4}{Q_2 B_1 + Q_2 B_2} \cdot \dot{T} \qquad (10)$$

where $B_3 = E_1/RT^2$ and $B_4 = E_2/RT^2$. To obtain Eq. (10), q_1 is expressed by means of q and $\dot{q}$ from Eq. (9).

If a set of n experiments are performed at different heating rates and analogously to [1], an isothermal section is made at $T = T_x$, passing thereby from non-isothermal kinetics to isothermal kinetics, a system of equations of the type Eq. (10) is obtained for each T_x value, where all B_i values will already be constants. In this case the relationship $[\ddot{q}/\dot{q}]_{T=T_x}$ vs. $(\dot{T})_{T=T_x}$ should be linear, and the fact that such linearity exists serves as the criterion for the fact that parallel reactions proceed.

The further determination of kinetic constants is as follows. If two isothermal sections are made at T_1 and T_2, the following system of equations is obtained:

$$\alpha_1 = B_1(T_1) + B_2(T_1)$$

$$\alpha_2 = B_1(T_2) + B_1(T_2)$$

$$\beta_1 = \frac{Q_1 B_3(T_1) B_1(T_1) + Q_2 B_4(T_1) B_2(T_1)}{Q_1 B_1(T_1) + Q_2 B_2(T_1)} \qquad (11)$$

$$\beta_2 = \frac{Q_1 B_3(T_2) B_1(T_2) + Q_2 B_4(T_2) B_2(T_2)}{Q_1 B_1(T_2) + Q_2 B_2(T_2)}$$

where β_1 and β_2 are the slopes of the lines $(\ddot{q}/\dot{q}) - \dot{T}$ vs. T_1 and T_2, respectively and α_1 and α_2 are the absolute values of the intercepts on the ordinate. Through the expression of K_1 and K_2 from the first two equations of the system (11), their substitution into the second two equations and then the expression of E_2 by E_1, a transcendent equation is finally obtained for the determination of E_1.

However, the relationship of the kinetic parameters may be such that, by varying w in the experiments, one will not succeed in determining Q_1 and Q_2. In such cases, four isothermal sections at different T values should be made: thus, four algebraic equations for α will be obtained in (11), and their numerical solution will allow the determination not only of K_1, K_2, E_1 and E_2, but also (by substituting the values obtained into the values for β in (11) the unknown thermal effects of the reaction.

If one of the reactions (e.g. the second) is thermally neutral, the indirect criterion for this being the change of q_∞ when w is varied from some value to zero, Eq. (10) will assume the following form:

$$\frac{\ddot{q}}{\dot{q}} = B_3\dot{T} - (B_1 + B_2) \tag{12}$$

In this case, if a set of experiments are carried out at different w values, isothermal sections are made at $T = T_x$ and the relationship $(\ddot{q}/\dot{q})_{T=T_x}$ vs. $\dfrac{1}{RT^2}(\dot{T})_{T=T_x}$ is plotted a straight line is obtained whose slope is E_1 and the intercept on the ordinate is α. Then if three isothermal sections are made, a system of three equations for will be obtained, analogous to the first two equations in (11), where E_1 is known. If K_1 and K_2 from the first two equations are substituted into the third, a transcendent equation is obtained for the determination of E_2:

$$(\alpha_1 e^{E_1 d} - \alpha_2)e^{E_2 P} + (\alpha_2 - \alpha_1 e^{E_2 d})e^{E_1 P} = \alpha_3(e^{E_1 d} - e^{E_2 d}) \tag{13}$$

where $d = (T_2 - T_1)/RT_1 T_2$; $p = (T_3 - T_1)/RT_1 T_3$.

Thus, owing to the kinetic connection between the reactions, in this case too, it is possible to utilize the experimentally obtained integral signal to determine the parameters of a reaction taking place without a thermal effect, i.e. a reaction that could not be studied directly.

Figure 3 presents the results of checking the above scheme for determining kinetic parameters by means of a computerized experiment with the above-cited kinetic parameters. The heating rate w was varied from 3 to 20 deg/min. On reduction to
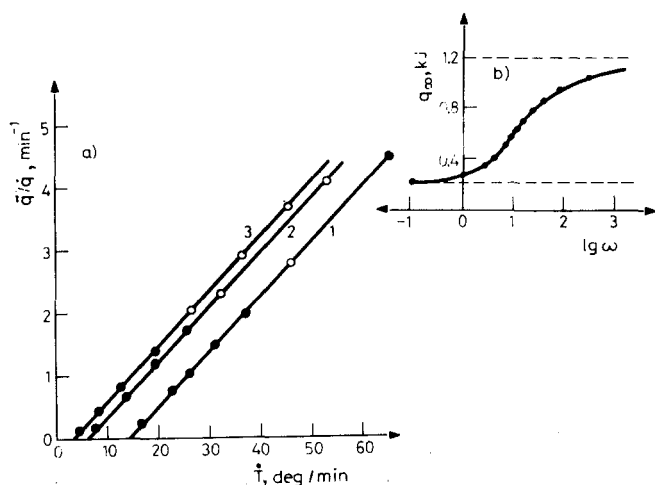

Fig. 3 Processing of kinetic information under non-isothermal conditions for parallel reactions. (a) Relationship $\ddot{q}/\dot{q}$ vs. $\dot{T}$; (1) 450 K; (2) 460 K; (3) 470 K . . linear heating, heating rate $w = 5$ deg/min,   ○ parabolic   heating, $w = 5$ deg/min $+ At$, $A = 2$–10 deg/min^2; (b) relationship q_∞ vs. ln w

isothermal conditions, a linear relationship $(\ddot{q}/\dot{q})$ vs. $\dot{T}$ was obtained, confirming that parallel reactions takes place. The relationship $q_{\infty}(w)$ presented in Fig. 3b also demonstrates this fact; the asymptotes at low and high w values allow the determination of the values of Q_1 and Q_2. Processing of the straight lines in Fig. 3a according to the above-described scheme yielded the values $E_1 = 39.80$ kJ/mol, $E_2 = 166.76$ kJ/mol, $K_1 = 0.48 \cdot 10^4$ min^{-1} and $K_2 = 0.26 \cdot 10^{19}$ min^{-1}. In addition, as demonstrated in Fig. 3a, the suggested calculation scheme is applicable to any heating regime, not only linear heating, if the value of T involved in the equation is determined experimentally.

Independent reactions

If q_2 is substituted by means of q and q_1 in Eq. (2) and its second derivative is taken with respect to time, the following equation is obtained for $\ddot{q}$:

$$\frac{\ddot{q}}{q_{\infty} - q} = B_1 B_2 + B_1 B_2 \left(\frac{B_3 - B_4}{B_2 - B_1}\right) \dot{T} - (B_1 + B_2) \frac{\dot{q}}{q_{\infty} - q} +$$

$$+ \frac{B_2 B_4 - B_1 B_3}{B_2 - B_1} - \frac{\dot{q}\dot{T}}{q_{\infty} - q} \tag{14}$$

Before turning to the determination of the kinetic parameters, let us consider the method for identifying independent reactions. If a set of n experiments are carried out at different heating rates w and isothermal sections $T_x = $ const. are made, n linear algebraic equations of the following type are obtained for this temperature:

$$a_i = A_3 + A_4 b_i - A_2 c_i + A_1 d_i \tag{15}$$

where $A_1 = B_1 B_2$; $A_2 = B_1 + B_2$; $A_3 = B_1 B_2 (B_3 - B_4)/(B_2 - B_1)$; and $A_4 = (B_2 B_4 - B_1 B_3)/(B_2 - B_1)$ are all constants. The experimentally obtained coefficients $a_i = \ddot{q}_i/(q_{\infty} - q_i)\dot{T}_i$; $b_i = \dot{q}_i/(q_{\infty} - q_i)$; $c_i = \dot{q}_i/\dot{T}_i$ and $d_i = 1/T_i$ correspond to $T = T_x$.

It can then readily be shown that a linear relationship $\varphi_i = A_1 - A_2 f_i$ must exist, where

$$\varphi_i = \frac{(a_i - a_{i+1})(b_i - b_{i+2}) - (a_i - a_{i+2})(b_i - b_{i+1})}{(d_i - d_{i+1})(b_i - b_{i+2}) - (d_i - d_{i+2})(b_i - b_{i+1})}$$

$$f_i = \frac{(c_i - c_{i+1})(b_i - b_{i+2}) - (c_i - c_{i+2})(b_i - b_{i+1})}{(d_i - d_{i+1})(b_i - b_{i+2}) - (d_i - d_{i+2})(b_i - b_{i+1})} \tag{16}$$

The slope of the linear relationship yields A_2, while the intercept on the ordinate yields A_1. This linearization in itself is proof that independent reactions take place.

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If A_1 and A_2 determined in this manner, for B_1 and B_2 the relationship $B_{1,2} = \dfrac{A_2 \pm \sqrt{A_2^2 - 4A_1}}{2}$ is obtained, and subsequently, if the function $\ln\, B_i(1/T_x)$ is plotted, the kinetic parameters of the individual stages will be obtained.

Successive reactions

For this case, the following equation is obtained for $\ddot{q}$:

$$\frac{\ddot{q}}{q_\infty - q} = B_1 B_2 - (B_1 + B_2)\frac{\dot{q}}{q_\infty - q} - \frac{B_1 B_3 - \dfrac{Q_1 + Q_2}{Q_1}B_2 B_4}{\left(\dfrac{Q_1 + Q_2}{Q_1}B_2 - B_1\right)} \cdot \frac{\dot{q}\dot{T}}{q_\infty - q} +$$

$$+ \frac{B_1 B_2 (B_3 - B_4)}{\dfrac{Q_1 + Q_2}{Q_1}B_2 - B_1} \cdot \dot{T} \tag{17}$$

which is similar to Eq. (14), except that Q_1 and Q_2 are involved. If these values are unknown, then (similarly as in the case of independent reactions) it is indispensable to make a series of isothermal sections at different T_x values and, from the values of A_1 and A_2 found at these temperatures, to determine $B_1(T_x)$ and $B_2(T_x)$; it is then easy to find the required parameters graphically. To determine Q_1 and Q_2, any of the algebraic equations of the type of Eq. (15) can be taken, with A_3 and A_4 having the following forms:

$$A_3 = \frac{B_1 B_2 (B_3 - B_4)}{\left(\dfrac{Q_1 + Q_2}{Q_3}B_2 - B_1\right)}$$

$$A_4 = \frac{\dfrac{Q_1 + Q_2}{Q_1}B_2 B_4 - B_1 B_3}{\dfrac{Q_1 + Q_2}{Q_1}B_2 - B_1}$$

where the B_1 and B_2 values used have previously been determined, and

$$\frac{Q_1 + Q_2}{Q_1} = \frac{q_x}{A_0 Q_1} \quad \text{and} \quad Q_2 = \frac{q_\infty}{A_0} - Q_1.$$

Linearization in the coordinates $\varphi_i\,(f_i)$ is characteristic for both independent and

successive reactions. Therefore, after linearization, to ascertain what reactions take place, the values of A_1, A_2 and A_3 must be determined, and the values of B_i found from $A_1(T_x)$ and $A_2(T_x)$, and substituted, for instance, into the relationship $A_3 = B_1 B_2 (B_3 - B_4)/(B_2 - B_1)$. If this is satisfied, the reactions are independent; if not, they are successive.

Figure 4 presents the results of a computerized kinetic experiment processed by the above-described scheme with the same initial kinetic parameters, for successive reactions. The thermal curves obtained in the calculation for programmed heating rates w from 3 to 40 deg/min yielded a single peak, i.e. from the shape of the thermal curves one cannot judge whether the process involves one or more stages. On passing to isothermal conditions, linearization is obtained in the coordinates $\varphi_i(f_i)$, demonstrating that successive reactions occur. Subsequent processing of the data yields the kinetic parameters of the individual stages with good accuracy (the error in the activation energy determination is below 10%).
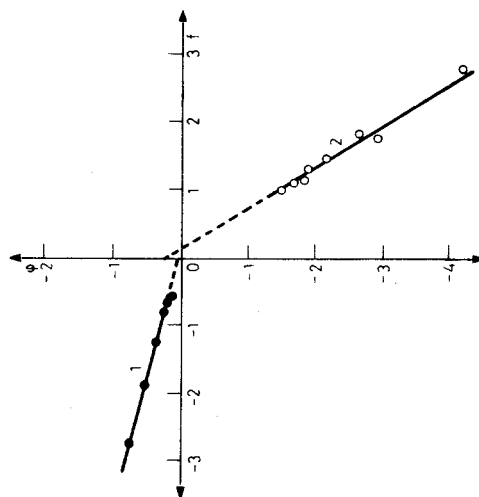

Fig. 4 Shape of the function $\varphi_i(f_i)$ for successive reactions (1) 455 K; (2) 475 K

Thus, the computerized kinetic experiments demonstrated that the suggested calculation schemes for the determination of kinetic parameters for the simplest two-stage reactions, are readily applicable under both isothermal and non-isothermal conditions. The main advantage of the method consists in the fact that there is no need for separation of the individual stages; kinetic information is obtained on the basis of the initial integral thermoanalytical data. As concerns the accuracy and reliability of the results, these depend on the accuracy of the experiment and on the accuracy of the subsequent processing of the experimental

data, particularly when the value of $\ddot{q}$ is to be obtained. It should be noted that the methods developed for numerical derivation [6] allow a satisfactory accuracy of this process. To establish the effect of the accuracy of the experimental data on the reliability of the kinetic information obtained, a special analysis was carried out on the example of two parallel reactions proceeding under isothermal conditions. The initial kinetic parameters were $K_1 = 10^{10}$ min^{-1}, $K_2 = 2 \cdot 10^6$ min^{-1}, $E_1 = 83.80$ kJ/mol, $E_2 = 50.28$ kJ/mol, $Q_1 = 838$ kJ/kg and $Q_2 = 1267$ kJ/kg. It was assumed that the initial experimental data ($\dot{q}, q$) were obtained with an error of $\pm 5\%$, this value being substantially higher than the values in the best certificates of modern thermoanalytical instruments ($\simeq 1\%$). The values of the determined kinetic parameters were within the following limits: $K_1 = 2.5 \cdot 10^9 – 4.4 \cdot 10^{10}$ min^{-1}, $K_2 = 5.1 \cdot 10^5 - 5.7 \cdot 10^6$ min^{-1}; $E_1 = 77.09 - 90.92$ kJ/mol; and $E_2 = 46.09 – 53.62$ kJ/mol. These data demonstrate that the method suggested for processing the experimental data is satisfactorily resistant to the experimental errors.

Finally, it should be noted that the method developed for determination of the kinetic parameters of two-stage reactions is readily applicable to thermogravimetric experimental data [7]. In this case, instead of q, q_∞ and $\dot{q}$, the momentary and final mass changes Δm and Δm_∞ and the mass change rate $\Delta \dot{m}$ are utilized in the calculations, and instead of Q_1 and Q_2, the molecular masses of the gaseous reaction products M_1 and M_2. It should also be pointed out that the suggested method may prove useful for the calculation of kinetic data in two-stage processes with more complicated stages (biomolecular, reversible, etc. processes), or in processes with more than two stages.

Conclusions

1. A method is suggested for processing thermoanalytical experimental data obtained under isothermal and non-isothermal conditions, allowing determination of the kinetic parameters of two-stage processes.

2. Complex parameters were developed for parallel, independent and successive reactions: processing of the experimental data in terms of these parameters allows establishment of the type of reaction and determination of the kinetic parameters of the individual stages.

3. Computerized kinetic experiments demonstrated that the suggested schemes are well suited for the determination of kinetic parameters.

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Zusammenfassung — Eine Methode zur Untersuchung der kinetischen Parameter von Zweistufenreaktionen unter Verwendung experimenteller thermoanalytischer Daten wird vorgeschlagen. Die Methode ermöglicht, die kinetischen Kennwerte des Prozesses basierend auf integralen thermoanalytischen Werten ohne Trennung der individuellen Schritte zu bestimmen. Unter isothermen und nicht-isothermen Bedingungen parallel, unabhängig voneinander und nacheinander verlaufende Reaktionen werden diskutiert.

Резюме — Предложен метод изучения кинетических параметров двухстадийных реакций по данным термоаналитического эксперимента. Метод позволяет определять кинетические характеристики процесса на основании интегральных термоаналитических данных, без последовательного выделения отдельных его стадий. Рассмотрены параллельные, независимые и последовательные реакции, протекающие в изотермических и неизотермических условиях.