EVALUATION OF KINETIC PARAMETERS AND MECHANISMS OF COMPLEX REACTIONS FROM THERMAL ANALYSIS DATA

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A method is for TA data-processing: the method of exponential multipliers (MEM). The application of this method permits determination of the steps of the process, the type of the kinetic function, the type of the reaction and the kinetic parameters of the reaction steps. The method is simple and is easily carried out with the use of a mini-computer. The efficiency of the method is illustrated on the example of the thermal decomposition of ammonia copper chromate. The mechanism of the process and the kinetic constants were determined. They agree with available literature data.

The reaction

$$A \xrightarrow{K} B \qquad (1)$$

proceeding under controlled heating is described by the folowing system of differential equations:

$$\dot{\eta} = K(T) f(\eta) \qquad (2)$$

$$cM \Delta \dot{T} = m_o Q \dot{\eta} - \alpha(T) S \Delta T,$$

$$\Delta T(0) = 0, \quad \eta(0) = 0, T_c = T_o + \varphi(w, t), \quad \eta = \frac{m_o - m}{m_o}$$

where η is the depth of conversion, ΔT is the temperature difference be-

tween the 'reactor' cell (T) and the 'witness' cell (T_e), M and c are the total mass and the heat capacity of the inert and the cell, m is the mass of the substance in question, Q is the reaction thermal effect (per mass unit),

$K(T)=k_o \exp(-E/RT)$, where k_0 is the pre-exponential factor and E is the activation energy, $\alpha(T)$ is the heat-transfer coefficient, S is the ampoule surface, T_c is the furnace teperature, T_0 is the initial temperature, and $\varphi(w,t)$ is the function setting the heating law.

Linear heating is the most popular, when $\varphi(w,t) = wt$ (w is the heating rate).

Determination of the type of the kinetic function $f(\eta)$, the kinetic parameters of k_0, E and the reaction thermal effect Q is necessary to solve the inverse problem.

The type of the kinetic function is usually set before hand. Researchers differ in their methods of determining the kinetic parameters. The first approach is to solve multiply primal problems, e.g. minimizing the sum of standard deviations of calculated values from experimental ones. In spite of its universality, this approach requires much computation time and does not solve the problem even in the most common cases.

Thus, a two-step first-order consecutive reaction is studied in [1]. For isothermal reactions, when the analytical solution of the corresponding system of equations is written down, and therefore the solution of the inverse problem is particularly simple, the constants cannot be obtained by this method.

Another approach is to rectify the experimental data [2] in the coordinates $(1/T, \ln[\dot{\eta}/f(\eta)])$.

The drawback of this method (even when the type of the $f(\eta)$ function is set correctly) is that, due to the strong Arrhenius dependence of the reaction rate on the temperature, the rectifications itself depends weakly on the $f(\eta)$-function type, and thus the correctness of the parameter determination is doubtful.

Method of exponential multipliers (MEM)

We suggest that the Arrhenius dependence of the reaction rate on the temperature be excluded by the method of exponential multipliers (MEM). Its essence lies in the following. Let the $\dot{\eta}(t)$ dependence be known experimentally. Let us multiply this curve by $\exp(\lambda/RT)$. The zero-order approximation for E is taken as λ. It can be completely rough.

When $\lambda > E$, the product $\dot{\eta}$ $\exp(\lambda/RT)$ decreases with temperature increase, and when $\lambda < E$, the product increases as the temperature increases for the initial curve fraction. Variation of λ which is easily performed automatically, permits determination of the activation energy with any accuracy assigned in advance.

Knowing the activation energy, we can proceed to the determination of the reaction mechanism. The first equation of system (2) may be rewritten as

$$k_0 f(\eta) = \dot{\eta} \exp(E/RT) \tag{3}$$

Since all values in the right-hand term of Eq. (3) are known at any t value (3) gives $k_0 f(\eta)$ as a time function. The dependence $\eta(t)$ is also known experimentally. Therefore, $k_0 f(\eta)$ is a function of the conversion depth.

Let us select the interpolation function for working out the following dependence:

$$A \eta^m (1-\eta)^n [-\ln(1-\eta)]^1$$

(this is the general type of the $f(\eta)$ function for solid-state reactions [3]) and find k_0 and $f(\eta)$.

Since the method employs two main operations, multiplication by the exponential curve and selection of the interpolation function, it is easily performed by a minicomputer and may serve as an express method.

Complex reactions are of special interest.

Each multistep reaction incorporates a great number of concurrent and consecutive steps. First, let us study the singularities of the inverse problem solution for the simplest two-step reactions.

Material decomposition by two concurrent reactions

Material decomposition by two concurrent reactions according to the scheme

$$
A
\begin{array}{c}
\overset{K_1}{\nearrow} B \\
\underset{K_2}{\searrow} C
\end{array}
\tag{4}
$$

is described by the following system of differential equations:

$$\dot{m} = -K_1(T)f_1(m) - K_2(T)f_2(m) \tag{5}$$

$$cM\Delta T = \sum_{i=1}^{2} Q_i K_i(T)f_i(m) - \alpha(T)S\Delta T,$$

$$\Delta T(0) = 0, \ m(0) = m_o, \ \Delta T = T - T_e$$

where $K_i(T) = k_i^0 \exp(-E_i/RT)$, $i = 1, 2$.

Let us assume that $\Delta T(t)$, $\Delta \dot{T}(t)$, $T_e(t)$, $m(t)$ and $\dot{m}(t)$ are known.

It follows from the reaction scheme that substance A changes completely into B or C, or partly into B and partly into C, depending on the rates of the reaction steps and the heating rate constants.

When both steps progress over the proximate temperature ranges and $K_1 \cong K_2$, the reaction may be considered simple. In that case, the kinetic equation is

$$\dot{\eta} = K_1(T)f(\eta)$$

where $f(\eta) = f_1(\eta) + f_2(\eta)$.

Therefore, let us study the case $K_1 \neq K_2$.

The thermal curve does not reveal whether one or two concurent reactions are taking place. Since a single substance is under going decomposition the thermal curve shows one thermal deviation peak, independently of the heating rate. However the net thermal effect, of the reaction, proportional to the area of the thermal effect, will be a function of the heating rate, because the thermal contribution of one or another reaction step changes simultaneously with the heating rate. This fact permits an unmistake ably identification of the decomposition process involving a number of concurrent steps.

An insignificant thermal contribution of one of the reaction steps and the impossibility of establishing the process complexity constitute no obstacle to successful solution of the problem.

The equality $\dot{m} \simeq -k_1^0 \exp(-E_1/RT)f_1(m)$ holds only for the initial curve fraction.

The MEM, i.e. multiplication of this equality by $\exp(\lambda/RT)$, gives E_1. Knowing the dependence of $k_1^0 f_1(m)$ on the mass, we find $f_1(m)$ and k_1^0. Expression

$$-k_2^0 \exp(-E_2/RT)f_2(m) = \dot{m} + k_1^0 \exp(-E_1/RT)$$

permits calculation of the kinetic parameters and the type of the second step kinetic function.

Figure 1 shows this technique for activation energy determination for decomposition by two concurrent first-order reactions with the equal pre-exponential factors and the activation energies $E_1 = 9400$ cal/mol; $E_2 = 12000$ cal/mol. (Calculations gave $9350 < E_1 < 9460; 11000 < E_2 < 12500$.)
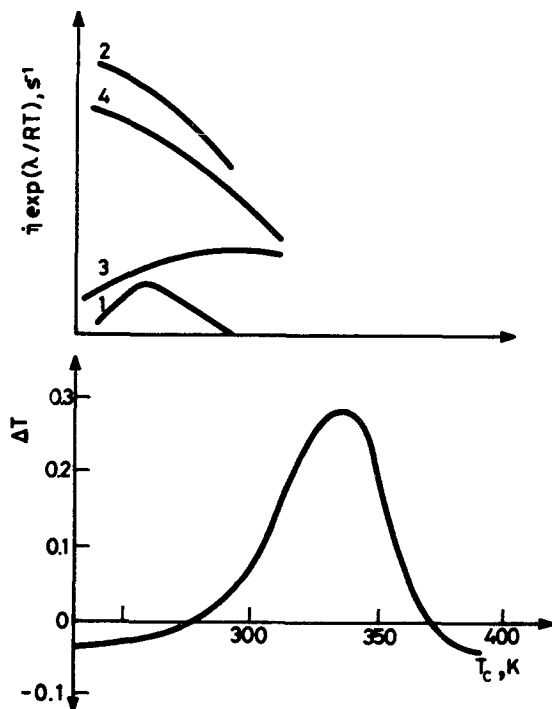

Fig. 1 DTA curve of decomposition of a substance in two concurrent reactions (bottom) application of MEM to each step; activation energy calculation when λ is: 1. 9350; 2. 9450; 3. 11000; 4. 12500 (above)

Consecutive reactions

Let us study a chemical reaction in which the starting substance is converted into the final product in two consecutive steps according to the following scheme:

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C \tag{6}$$

Process (6) is described by the following system of differential equations:

$$\dot{m}_1 = -K_1(T)f_1(m_1), \tag{7}$$

$$\dot{m}_2 = K_1(T)f_1(m_1) - K_2(T)f_2(m_2) \tag{8}$$

$$cM\Delta T = \sum_{i=1}^{2} Q_i K_i(T)f_i(m_i) - \alpha(T)S\Delta T \tag{9}$$

$$\Delta T = T - T_e, \ T_e = T_o + \varphi(w,t)$$

with the initial conditions $m_1(0) = m_1^o$, $m_2(0) = 0$ and $\Delta T(0) = 0$. Let us assume that $\Delta T(t)$, $\Delta \dot{T}(t)$, $T_e(t)$, $m_1(t)$, $\dot{m}_1(t)$ are known, where m_1 and m_2 are the masses of substances A and B, respectively. The mass of substance C, m_3, is calculated from the material balance condition $m_1 + m_2 + m_3 = m_1^o$.

With different relation constants for K_1 and K_2, reaction (6) progresses in different ways [4]. When $K_1 = K_2$, the thermal curve shows one peak of temperature deviation. If $K_1 > K_2$, the thermal curve may show two thermal effects, when the heating rate is reduced or the reaction mixture is deluted by an inert substance. When a quasi-stable area sets in between the peaks, each thermal effect may be processed by the methods developed for a simple single reaction. When $K_1 < K_2$, the thermal curve shows one peak of temperauture deviation. The intermediate has no time to accumulate. The product accumulation and flow rates are approximately equal. This permits application of the quasi-stable concentrations method, which simplifies the initial system of equations substantially. The reaction seems

to progress according to the scheme A → C. The starting substance changes into the final one with first reaction elementary constants k_1^0, E_1 and the net thermal effect $Q = Q_1 + Q_2$.

Thus, the case $K_1 > K_2$ is sufficient for consecutive reactions.

The values of E_1, k_1^0, and $f_1 (m_1)$ are determined from the $\dot{m}_1 (t)$ curve by the MEM, as was done for a simple single reaction. The net thermal effect is calculated from the area of the thermal effect. Then, employing the thermal balance Eq. (9), and assuming that

$$Q_1 K_1 (T) f_1 (m) \simeq cM\Delta\dot{T} + \alpha (T) S\Delta T$$

for the initial curve fraction, we find $Q_1 k_1^0$. This permits calculation of Q_1 and Q_2.

The second step kinetic parameters are found from the expression

$$K_2 (T) f_2 (m_2) = \frac{1}{Q_2} [cM\Delta\dot{T} + \alpha S\Delta T - Q_1 K_1 (T) f_1 (m)] \tag{10}$$
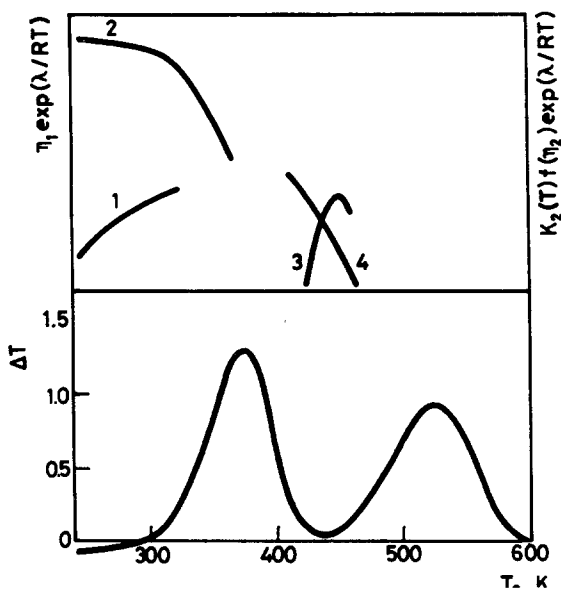

Fig. 2 DTA curve of two consecutive reactions (bottom); example of calculation of activation energy of the steps (above) when λ is: 1. 11000; 2. 12000; 3. 16000; 4. 17000

Multiplying Eq. (10) by exp (λ / RT), we get E_2 and then find the dependence of $k_2^0 f_2 (m_2)$ on time. Integrating Eq. (8), we get

$$m_2 (t) = -\int_0^t [\dot{m}_1 (t) + K_2 (T) f_2 (m_2)] \, dt \qquad (11)$$

Employing Eq. (11), we find the dependence of $k_2^0 f_2 (m_2)$ on m_2, which permits determination of $f_2 (m_2)$ and k_2^0.

Figure 2 shows the procedure of calculation E_1 and E_2 by the MEM, employing Eqs (7) and (10) for two-step first-order consecutive reactions, with E_1 = 11690 cal/mol; E_2 = 16700 cal/mol. (Calculations gave 11000 < E_1 < 12000; 16000 < E_2 < 17000.)

Independent concurrent reactions

A process with two independent concurrent reactions is described by the following scheme:

$$A \xrightarrow{K_1} C$$

$$B \xrightarrow{K_2} D \qquad (12)$$

Let m_1 and m_2 denote the masses of substance A and B, respectively. When the rate constants are equal, this process can be considered to be a simple single reaction with activation energy $E = E_1 = E_2$, the pre-exponent $k_o = k_1 = k_2^0$ and the net thermal effect $Q = Q_1 + Q_2$. When $K_1 \neq K_2$ for definiteness we assume that $K_1 > K_2$ separation of the reaction in time [5] by the heating rate variation may result in two temperature deviation peaks in the curve. When the rate of the first step is much higher than that of the second, the temperature deviation peaks are separated by a quasi-stationary areas in the thermal curve. Each peak can be processed separately.

Process (12) is described by the following system of differential equations:

$$\dot{m}_1 = -K_1(T)f_1(m_1), \tag{13}$$

$$\dot{m}_2 = -K_2(T)f_2(m_2), \tag{14}$$

$$cM\Delta\dot{T} = \sum_{i=1}^{2} Q_i K_i(T)f_i(m_i) - \alpha S\Delta T$$

$$\Delta T = T - T_e, \quad T_c = T_o + \varphi(w, t)$$

with the initial conditions

$$m_1(0) = m_1^o, \quad m_2(0) = m_2^o, \quad \Delta T(0) = 0$$

In this case,
$\Delta T(t)$, $\Delta \dot{T}(t)$, $m(t) = m_1(t) + m_2(t)$, $\dot{m}(t) = \dot{m}_1(t) + \dot{m}_2(t)$ are know experimentally.

The relation $\dot{m}(t) \simeq \dot{m}_1(t)$ is valid for the initial curve fraction. Multiplying by $\exp(\lambda/RT)$ (MEM), we find E_1, and then

$$k_1^o f_1(m_1) = \dot{m}_1 \exp(E_1/RT)$$

The dependence $m(t) \approx m_1(t) + m_2(0)$ is know experimentally. Hence, $k_1^o f_1(m_1)$ is defined as a function of $m_1 + m_2(0)$, which permits establishment of the mechanism of the first step. Thus, the dependence $\dot{m}_1(t)$ is found.

Employing the equality $\dot{m}_2(t) = \dot{m}(t) - \dot{m}_1(t)$, we find the kinetic parameters and the kinetic law of the second step. The net thermal effect Q is calculated from the area of the thermal effect. The thermal curve also permits determination of Q_1 and Q_2, since

$$Q_1 K_1(T)f_1(m_1) \approx cM\Delta\dot{T} + \alpha S\Delta T$$

for the initial curve fraction. Therefore, it permits determination of $Q_1 k_1^o$ and thus Q_1 and Q_2.

Equation (13) must be integrated immediately after the desired values are determined, in order to differentiate the concurrent and consecutive reactions. We get the starting mass of the substance in question when the

reactions are consecutive. In the opposite case, we get the independent concurrent reactions.

Application of MEM to the experimental data processing schedule

Application of the method to cases (1), (4), (6) and (12) was shown above.

The problem solution incorporates the following steps (operation results are given in parenthesis):

a) application of MEM to $\dot{m}$ (E_1, k^o, f_1);

b) application of MEM to

$$F(T) = (cM\Delta\dot{T} + \alpha S\Delta T) = \sum_{i=1}^{2} Q_i K_i f_i (m_i) \quad (E_1, Q_1, k_1^o, f_1);$$

c) calculation of the area of the thermal effect

$$Q = \frac{1}{m_o} \int_0^\infty (\alpha S\Delta T) \, dt;$$

d) application of MEM to

$$Q_2 K_2 f_2 = [cM\Delta\dot{T} + \alpha S\Delta T - Q_1 K_1 f_1] \quad (E_2, Q_2, k_2^o, f_2);$$

e) application of MEM to $K_2 f_2 = \dot{m} + K_1 f_1$ (from Eq. (5)); (E_2, k_2^o, f_2, Q_2);

f) integration of $\dot{m}_1$ (m_1) (from Eq. (7) or (13));

g) integration of $\dot{m}_2$ (m_2) (from Eq. (8) or (14)).

Let us assign the sequence of operations for each reaction (1), (4), (6) and (12):

(1) $a (E, k_o, f)$, $d (E, Qk_o, f, Q)$, $b (Q)$;

(4) $a (E_1, k_1^o, f_1)$, $d (E_1, Q_1 k_1^o, f_1, Q_1)$, $b (Q)$, $c (E_2, Q_2 k_2^o, f_2)$,
$\quad g (E_2, k_2^o, f_2, Q_2)$

(6) $a (E_1, k_1^o, f_1)$, $d (E_1, Q_1 k_1^o, f_1, Q_1)$, $b (Q, Q_2)$, $c (E_2, Q_2 k_2^o, f_2, k_2^o)$
$\quad f (m_2)$;

(12) $a\,(E_1, k_1^0, f_1)$, $d\,(E_1, Q_1\,k_1^0, f_1\,Q_1)$, $b\,(Q, Q_2)$, $e\,(m_1)$,

   $c\,(E_2, Q_2\,k_2^0, f_2, k_2^0)$, $f\,(m_2)$.

The following operations are necessary to detemine the desired values and functions.

An experiment incorporating different heating rates and dilution of the starting substance by an inert substance will be useful for obtaining the information about the complexity of the process.

When such information is obtained, i.e. the thermal curve shows two peaks of temperature deviation, the sequence of reasoning becomes shorter, due to the possibility of scheme (6) or (12).

Applying the MEM to the kinetic curve, we find the first step activation energy E_1 (stage 'a' in our schedule). Multiplying $\dot{m}$ by $\exp(E_1/RT)$, we exclude the temperature-dependence for the initial curve fraction and are able to determine the mechanism of the first step of the reaction.

From the $\dot{\eta}\exp(E_1/RT)$ $vs.\,\eta$ $[\eta = (m_o - m)/m_o]$ plot we determine not only the mechanism, but also the reaction type. Figure 3 shows plots of the consecutive and independent concurrent reaction phase-plane patterns (schedules (6) and (12)) against the heating rate, illustrated by the first-order reactions $(f(\eta) = 1 - \eta)$.

The Figures show normalized values of the function $\dot{\eta}\exp(E_1/RT)$ plotted on the ordinate-axis. Max $\dot{\eta}\exp(E_1/RT)$ is employed as the normalization factor. The relation between $\dot{\eta}\exp(E_1/RT)$ and η is independent of the heating rate for consecutive reactions. Due to the experimental measurements of the rate of initial material consumption, the phase-plane pattern gives the first step kinetic function, independently of the heating rate.

At low heating rates, the second step of the independent concurrent reaction originates when the starting substance of the first step has burnt out. The early origin of the second step of the reaction depends on the heating rate increase.

The phase-plane pattern of the first kinetic function is distorted when the conversion is lower (curves 2 and 3). When the reaction type is defined, the treatment is carried out according to this type of reaction processing schedule (in this case scheme (6) or (12)).

The dependence of the area of the thermal effect on the heating rate is another characteristic which facilitates the further solution of the problem. In this case, it can be stated that the process represents the decomposition
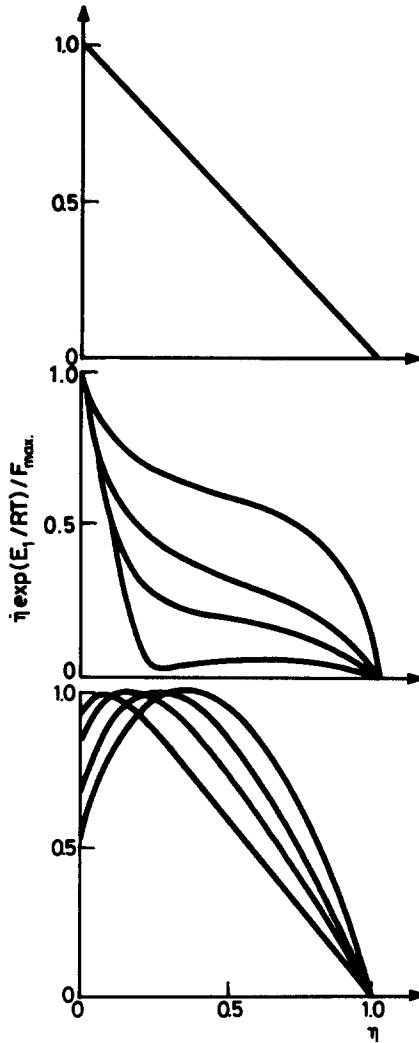
Fig. 3 Phase-plane patterns of consecutive, independent and concurrent first-order reactions, respectively at different heating rates; curves 1, 2, 3 and 4 are arranged in order of ascending w

of substance in concurrent steps and the treatment is carried out in accordance with schedule (4).

As mentioned above, we obtain E_1 by applying the MEM to the kinetic curve and plot $\dot{\eta}\exp(E_1/RT)$ vs. η. Figure 3 shows the plot of this dependence as a function of the heating rate for two concurrent first-order reac-

tions. For concurrent reactions, the type of the first step kinetic function may be determined only by shifting the equilibrium towards this step, i.e. decreasing the heating rate or diluting the starting mixture with an inert substance.

Figure 3 shows that the information relating to the complexity and type of the process can be obtained from the $\dot{\eta} \exp(E_1 / RT)$ *vs.* η curve.

Thus, when there is no change for a multiple experiment by varying the heating rate or diluting the starting substance with an inert substance, the type of the reaction can be determined from the phase-plane pattern., i.e. the application of the MEM permits calculation of the kinetic parameters, the kinetic function and reaction type.

Figure 4 shows the sequence of operations chart for processing the thermoanalytical experimental data.
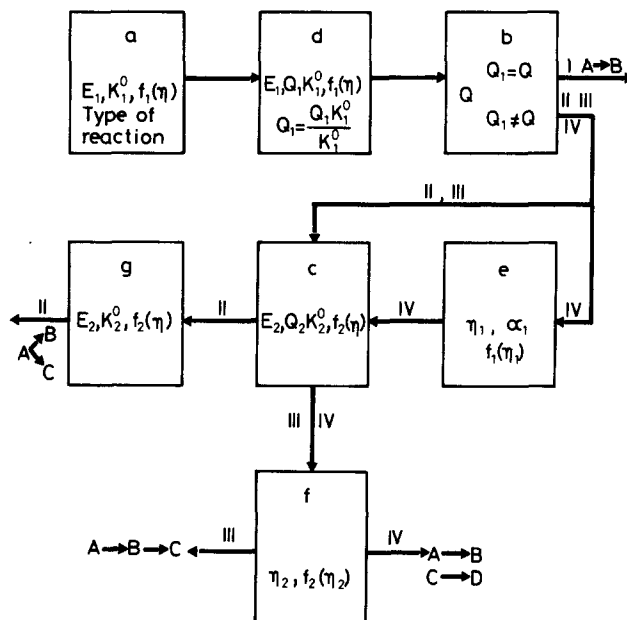

Fig. 4 Schematic representation of operation sequence for data-processing of thermoanalytical experiment

Application of MEM to multistep reactions

It must be mentioned that the MEM can be applied not only to two-step, but also to multistep reactions. Once the reaction first-step kinetic parameters and the link type of the subsequent reaction have been determined, the kinetic and the temperature kinetic curves for the remaining (n-1) steps are constructed. Applying the MEM to these curves, we determine the second-step parameters and the link type of the subsequent reaction, etc. Thus, in general, the kinetic parameters of a multistep reaction with either identical or different link types can be calculated by means of the MEM. The time and temperature of the beginning of the i+1th can be calculated from the dependence of $\dot{\eta}_i \exp(E_1/RT)$ on η_i. Application of the MEM to the initial step of the process in question, where the kinetic function transformation is insignificant and the thermal contribution is small, increases the accuracy of the kinetic parameter calculation.

Thermal decomposition of ammonia copper chromate

Let us illustrate the application of the MEM on the example of the thermal decomposition of ammonia copper chromate (ACC). The ACC decomposition data are taken from [6]:

$E_1 = 28$ kcal/mol; $E_2 = 26.5$ kcal/mol; $k_1^0 = 5.10^7$ s^{-1};

$k_2^0 = 6.3 . 10^8$ s^{-1}; $f_1(\eta) = 1 - \eta$; $f_2(\eta) = \eta(1 - \eta)$. The mixture is diluted

with alumina in 1:100.

The thermal curve shows one temperature deviation peak at any heating rate.

The area of the thermal effect is practically independent of the heating rate. Application of the MEM to the kinetic curve gives $E_1 = 27800$ cal/mol (0.7 % error). The $\dot{\eta} \exp(E_1/RT)$ vs. depth of conversion curve is plotted (see Fig. 5). The form of the curve indicates the degree of complexity of the reaction, at least weather it is a two-step one. The type of interactions of the steps is concurrent. The insignificance of the thermal contribution indicates that this is the initiation reaction, while the basic process is implemented by the second reaction.
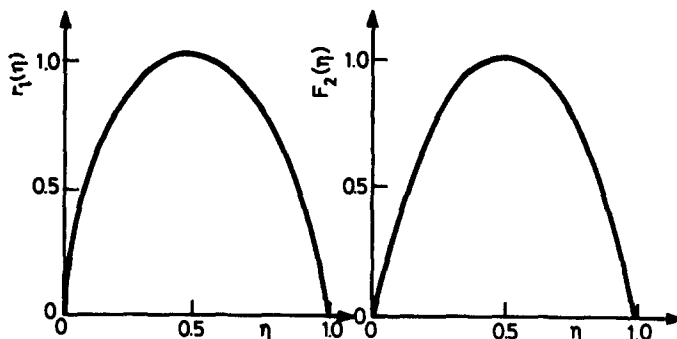
Fig. 5 $F_1(\eta) = F_1(T) \exp(E_1/RT)$ and $F_2(\eta) = F_2(T) \exp(E_2/RT)$ dependences for ACC

The pre-exponent value k_1^0 equals $4.10^7 \, s^{-1}$ (20 % error), $f_1(\eta) = 1 - \eta$. To determine the thermal effect of the rection, we   calculate the MEM parameters, E_1, Qk_0 and f_1, from the temperature curve

$$F(T) = cM\Delta\dot{T} + \alpha S\Delta T, \quad Q_1 = Qk_0 / k_1^0 \cong 69.9 \, \text{cal/g}$$

The curve is thenprocessed by the MEM.

$$F_2(T) = Q_2 K_2 f_2(\eta) = F(T) - Q_1 K_1 f_1(\eta) \tag{15}$$

The $F_2(T) \exp(\lambda/RT)$ curve rises with temperature, at any value of λ. This means that the function $f_2(\eta)$ vanishes when $\eta = 0$ and the exponential curve is unable to 'lift' it. To eliminate zero, we must divide Eq. (15) by η^m (m = 1/2, 2/3, 3/4, 1). In the case in question, η acts as the divisor. Now, E_2 may be   found by the MEM. We get the activation energy $E_2 = 24500$ cal/mol (0.8 % error). The $Q_2 k_2^0 f_2(\eta)$ function phase-plane pattern shows that the reaction is self-accelerating ($f_2(\eta) = \eta(1 - \eta)$), and has no more steps,or the second and third steps interact consecutively. The reaction heat Q determined solves the problem.Application of the MEM to the kinetic curve $K_2 f_2 = \dot{\eta} - K_1 f_1$ gives $k_1^0 = 1.10^8 \, s^{-1}$ (84% error). The thermal efect of the second step $Q_2 = Q_2 k_2^0 / k_2 \cong 70.6$ cal/g (1.4% error). The reaction heat Q calculated from the area of the thermal effect, is 69.7 cal/g. The solution

of the direct problem with the calculated parameters gives the same value of
Q. Hence, the process has two steps.

The MEM permits calculation of the kinetic parameters with sufficient
accuracy. Pre-exponential factors are the worst to calculate, but the system
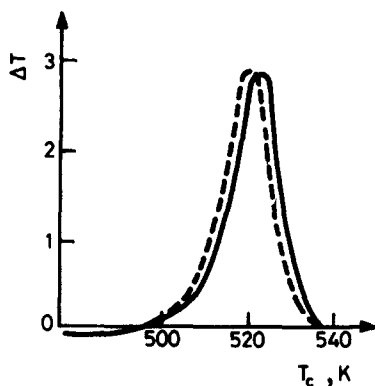is insensitive to these errors.

Fig. 6 Dependence of temperature deviation peak on temperature for ACC. The solid curve is
constructed from the numerical experimental data; the dashed one is plotted from the
solution parameters of the inverse problem.

Figure 6 shows a comparison of the experimental curve with that con-
structed from the solution parameters of the inverse problem. The curve is
shifted along the media temperature. The displacement constitutes 0.8%,
i.e. it is equal to the error in the calculation of the activation energy of the
reaction steps. The displacement of the curves to the left was explained by
the deficiency in the calculation of the constants. Instrumental errors were
not evaluated. This is a task for future experiments.

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Zusammenfassung — Ein Verfahren zur Verarbeitung von TA-Daten wurde entwickelt: das Verfahren exponentieller Multiplizierglieder (MEM). Die Anwendung dieses Verfahrens erlaubt die Bestimmung der Schritte eines Vorganges, des Typs der kinetischen Function, des Reaktionstypes und der kinetischen Parameter der Reaktionsschritte. Es handelt sich um eine einfache Methode, die auf einem Mini-Computer leicht verwirklicht werden kann. Die Wirksamkeit dieses Verfahrens wird am Beispiel der thermischen Zersetzung von Ammoniumkupferchromat gezeigt. Der Mechanismus und die kinetischen Konstanten des Prozesses wurden bestimmt, sie stimmen mit erreichbaren Literaturdaten überinen.