

## THEORETICAL DEVELOPMENT OF NONISOTHERMAL METHODS APPLIED FOR CHEMICAL REACTION INVESTIGATIONS: SOME ASPECTS RELATED TO SHS

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*The state-of-the art of nonisothermal methods applied for investigating a reacting substance is discussed. A new method is suggested for solving inverse problems of chemical kinetics which is referred to as the integral method of exponential factors (IMEF). Based on the IMEF, a set of programs is developed. A device-computer system is employed to study the chemical transformation processes underlying SHS*

**Introduction.** The works devoted to self-propagating high-temperature synthesis (SHS) may be arbitrarily grouped into two interrelated trends. The first, so-called technological, trend is deals with creation of new technologies for obtaining materials and articles on their basis. It has already been embodied in different technologies. The second trend comprises the works involved in research on the macrokinetic mechanism of processes occurring in a combustion wave and reaction products. The goal of this trend is to solve problems aimed at understanding SHS as a whole and individual physico-chemical stages. Here, chemical transformations are of importance because SHS is based on just these processes, which are its moving force.

A significant place in the development of this trend is occupied by mathematical simulation. Construction of the mathematical model of a chemical reaction requires not only an understanding of the chemistry of the process but also knowledge of the kinetic parameters of the reactions underlying the process. Therefore formulation and analysis of the inverse problems of chemical kinetics and use of their solutions to develop new calculation and experimental methods are of considerable importance.

Classical isothermal methods of kinetic studies are often inapplicable for investigating exothermic reactions in condensed media, especially in regimes important from theoretical and practical considerations, appropriate for a reaction to proceed in a combustion wave, as in the case of SHS. Such processes require nonisothermal methods for their investigation.

Reserachers from the Institute of Structural Macrokinetics of the Russian Academy of Sciences have developed the procedures for conducting a kinetic experiment, carried out a series of works in which methods of processing the data of a nonisothermal experiment are proposed for obtaining kinetic information both for simple and stepwise processes [1-4]. We can say with reasonable confidence that theoretical difficulties in the research on the kinetics of stepwise processes are overcome. Such methods as the method of exponential factors (MEF) and the integral method of exponential factors (IMEF) allow one to use a continuous time dependence of some process characteristic to completely solve the inverse problem for complicated reactions, i.e., to determine the type of interaction of the stages and the kinetic parameters and the mechanism of each stage. But the hardware for a nonisothermal experiment and its insufficient precision are still the basic challenge.

**Formulation of the Problem.** In developing the methods to solve inverse problems in the theory of nonisothermal processes, we have pursued the following goals:

1. The recent computerization of research studies and the availability of personal computers necessitate elaboration of methods for processing experimental data and for solving inverse problems with their use that make it possible to employ minicomputers.

2. A nonisothermal experiment is distinguished by simplicity, and therefore it needs simple methods for processing of its results.

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At present we can offer two approaches to the solution of inverse problems that are implemented in four different methods. The first approach is based on an approximate solution of the direct problem [3, 5]. In the present work, we consider the second approach, which has resulted in development of the MEF and IMEF. We will use simple reactions to illustrate the methods.

We assume conditions in the experiment for which the temperature in a substance succeeds in leveling off and becomes practically the same at all points of the reaction volume. Then a nonisothermal one-stage process may be described by the following system of differential equations:

$$C_p \dot{T} = \dot{q} - \alpha \frac{S}{V} (T - T_c), \quad \dot{\eta} = k^0 \exp(-E/RT) f(\eta), \quad T(0) = T_c, \quad \eta(0) = 0. \quad (1)$$

To solve the inverse problem, we must establish the form of the kinetic function  $f(\eta)$ , calculate the kinetic parameters  $E$ ,  $k^0$ , and determine  $Q$ .

**Method of Exponential Factors (MEF).** The method makes it possible to obtain kinetic information from any nonisothermal experiment in which the change of some process characteristic is continuously recorded. The MEF allows one to investigate both exo- and endothermic reactions, to carry out a process under both static (at a constant temperature of the medium, using only self-heating of the substance) and dynamic (with a change in the medium temperature) conditions. The MEF also makes it possible to establish the stepwise character of the process, the number of stages, the reaction type, and the form of the kinetic function at each stage, and to calculate kinetic parameters - all this being done without any suppositions about the mechanism of the process. In [1-3], the MEF as applied to thermal analysis is considered, in [3, 6] - to thermal and electrothermal explosion.

Let a process consist of a single stage. If in the experiment we measure the substance temperature vs time, then differentiating this dependence and using the heat balance equation (the first equation of system (1)), we arrive at  $\dot{q}(t) = C_p \dot{T} + \alpha S/V (T - T_c)$ . We will assume that  $C_p$  and  $\alpha S/V$  are known. In calorimetric and electrothermographic experiments the heat release rate  $\dot{q}(t)$  is measured immediately.

In order to determine the activation energy, we multiply  $\dot{q}(t)$  at each instant of time by  $\exp(\lambda/RT)$ , where  $\lambda$  is the zeroth-order approximation for the activation energy, which may be arbitrarily rough. If  $\lambda > E$  and the exponent is positive, the product  $\dot{q}(t) \exp(\lambda/RT)$  decreases with increase in temperature, and if  $\lambda < E$  and the exponent is negative, this product increases with increase in temperature on the initial section. Variation of  $\lambda$ , accomplished automatically, allows one to determine the activation energy to any prescribed accuracy.

Next, we eliminate the Arrhenius dependence of the reaction rate on temperature by multiplying it by  $\exp(E/RT)$ . From the area of the thermal curve we determine the thermal effect of the reaction  $Q = \int_0^\infty \dot{q}(\tau) d\tau$ . Since in the right-hand side of the expression  $k^0 f(\eta) = \dot{q} \exp(E/RT)/Q$  all the quantities are known for any  $t$ , it gives  $k^0 f(\eta)$  as a function of time. Having  $Q\eta(t) = q(t) = \int_{t_0}^t \dot{q}(\tau) d\tau$ , we find  $k^0 f(\eta)$  as a function of  $\eta$ . The curve in the phase plane is processed by methods traditional for chemical kinetics. We choose the form of the equation describing the curve and find the parameter  $k^0$ .

Thus, the MEF involves two basic operations, namely, multiplication by an exponent and choice of an interpolation function. It is easily realized on any computer, including a minicomputer used in the experiment.

The MEF as applied to research on stepwise processes is discussed in detail in [1-3], where model examples and solutions of particular problems are described.

Figure 1 illustrates determination by the MEF of the activation energy of a simple reaction substance decomposition in two parallel stages, and two successive reactions.

**Integral Method of Exponential Factors (IMEF).** This method eliminates the temperature dependence of the kinetic function  $\eta(t)$  rather than of the reaction rate, as in the case of the MEF. According to (1):

$$\eta(t) = k^0 \int_{t_0}^t \exp(-E/RT(\tau)) f(\tau) d\tau. \quad (2)$$

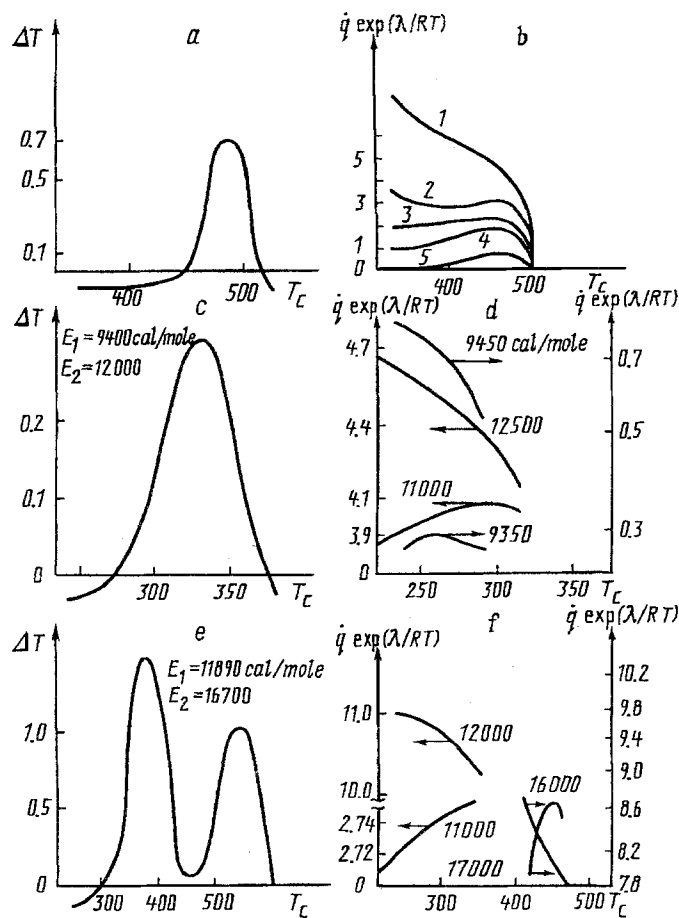


Fig. 1. DTA curves of thermal decomposition of pyroxylin (a), decomposition of the substance in two parallel stages (c), two successive reactions (e), and illustration of determination of the activation energy of the stages by the MEF (b, d, f); b: 1)  $\lambda = 48,000$  kcal/mole; 2) 47,500; 3) 47,200; 4) 46,500; 5) 40,000 kcal/mole.  $T_c$ ,  $^{\circ}\text{C}$ .

To determine the activation energy, we multiply the right-hand and left-hand sides of equality (2) by  $\int_{t_0}^t \exp(\lambda/RT(\tau))d\tau$ , where  $\lambda$  is an arbitrarily rough approximation for  $E$ .

It is easy to show that if the change in the kinetic function in the interval  $(t_i, t_{i+1})$  is insignificant, the product  $\eta(t) \int_{t_i}^{t_{i+1}} \exp(\lambda/RT(\tau))d\tau$  ( $t_i \leq t \leq t_{i+1}$ ) decreases with increases in temperature for  $\lambda > E$ , but for  $\lambda < E$  it increases.

Changing  $\lambda$ , we may find  $E$ .

This circumstance provides the basis for the algorithm and software used for determining the kinetics of reactions from the nonisothermal experiment [4].

The IMEF, possessing all the merits of the MEF, is free of its disadvantages. It does not need smoothing or differentiation of the experimental curves or a high accuracy of the experiment on the initial section, and it permits us to start processing from any section of an experimental curve. Also of benefit is that for the entire temperature interval considered the IMEF allows construction of a function of temperature, which we have called a diagnostic curve. This curve may answer the following questions: 1) whether we are concerned with a simple or complex reaction, 2) whether a time interval exists in which the process is accomplished in one stage, 3) whether the process is complicated by some other physical factor, 4) whether the inverse problem may be completely solved using available experimental data.

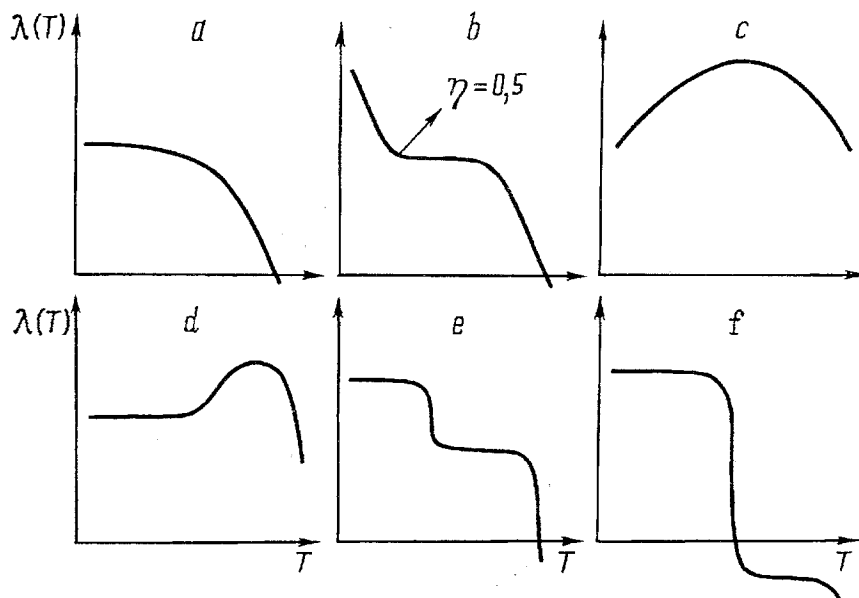


Fig. 2. Diagnostic curve of a single-stage process with  $f(\eta) = (1 - \eta)^n$  (a),  $f(\eta) = (1 - \eta)^n \eta^m$  (b), a two-stage process with inseparable stages (c), decomposition of a substance in competing parallel stages (d, e, f).

**Construction of the Diagnostic Curve.** We consider construction of the diagnostic curve for the example of TG and DTG curves ( $\eta(t)$  and  $\dot{\eta}(t)$ , respectively).

In the vicinity of any point  $\eta_0 = \eta(t_0)$  the curve may be approximated by the function

$$\eta(t) = \eta(t_0) + \int_{t_0}^t k(t_0) \exp(-\lambda(t_0)/RT(\tau)) d\tau \quad (k(t_0) = k^0 f(\eta(t_0)))$$

provided that  $\eta(t)$  differs slightly from  $\eta(t_0)$  and, correspondingly,  $\dot{\eta}(t) = k(t_0) \exp(-\lambda(t_0)/RT(t))$ .

Thus, the curve  $\eta(t)$  (if we use TG data) may be subdivided into the sections  $\eta_1 = \eta(t_1)$ ,  $\eta_2 = \eta(t_2)$ , ...,  $\eta_m = \eta(t_m)$  and, as it were, "glued together" from the curves

$$\eta_i + \int_{t_i}^t k(t_i) \exp(-\lambda(t_i)/RT(\tau)) d\tau,$$

while the curve  $\dot{\eta}(t)$  (if we deal with DTG data) may be approximated by a series of curves of the form  $k(t_i) \exp(-\lambda(t_i)/RT(t))$ . The process of performing such an approximation is analogous to the construction of splines. In complexity of realization, it is identical to any primary processing of experimental data and permits one to use different algorithms (approximating, smoothing, etc.) for its implementation.

Thus, from  $\eta(t)$  or  $\dot{\eta}(t)$  we obtain the diagnostic curve  $\lambda(t)$  or  $\lambda(T)$  (in temperature coordinates). If on some section the fraction  $\eta(t)$  satisfies the kinetic equation of system (1), then

$$\lambda(T) = E - \frac{RT^2}{T} f'(\eta) k(T) \exp(-E/RT), \quad k(T) = k^0 f(\eta).$$

For linear heating,  $T = \text{const} = \omega$ :

$$\lambda(T) = E \left[ 1 - f'(\eta) \int_0^\eta \frac{d\eta}{f(\eta)} \right].$$

From the form of the diagnostic curve we may judge the complexity of the process and the mechanism of the reaction. If  $f(\eta) = (1 - \eta)^n$ , then at small degrees of transformation  $\lambda(T) \approx E$  and the curve  $\lambda(T)$  has the form in Fig. 2a. For  $f(\eta) = (1 - \eta)^n \eta^m$  the curve  $\lambda(T)$  is depicted in Fig. 2b. When competing reactions participate in the process, the curve  $\lambda(T)$  behaves as in Fig. 2d, e, f. The concrete form of the curve depends on the temperature and

the degree of transformation at which the second stage becomes involved in the process. Figure 2c pertains to inseparable stages. Thus, rather simple processing of experimental data makes it possible to construct the function  $\lambda(T)$ , which distinguishes the leading stage and gives its activation energy and the preexponential factor. The kinetic function for known  $k^0$  and  $E$  is constructed in the traditional manner. The parameters of another stage in the case of a complex reaction are determined in a manner similar to [1-3].

**Error Estimation in Determination of Kinetic Parameters.** We estimate the error for the case of a single-stage process. The error depends on the relative error of the experiment and its temperature range.

The temperature range within which the activation energy and the preexponential factor are determined is  $[T_1, T_2]$  ( $T_1 < T_2$ ) with the assumption that at  $T_1$  the start of the process is already recorded. Then the error in determination of the activation energy  $\Delta E$  may be prescribed [4]:

$$\Delta E = \ln \frac{1 + \varepsilon}{1 - \varepsilon} \cdot \frac{RT_1 T_2}{T_2 - T_1}$$

or, assuming that  $\varepsilon$  is small,

$$\Delta E \approx 2\varepsilon RT_1 T_2 / (T_2 - T_1). \quad (3)$$

With the error of the activation energy  $\Delta E$ , the preexponential factor is determined with the relative error

$$\frac{\Delta k}{k} = |\exp [2\Delta E / R (T_1 + T_2)] - 1|. \quad (4)$$

These estimates are accurate in the sense that if we take, as the activation energy, any value from the interval  $(E - \Delta E, E + \Delta E)$ , with  $E$  being the true value of the activation energy, and recalculate the preexponential factor by formula (4), then the process may be described within the limits of the relative error  $\varepsilon$ .

From (3), it is easy to estimate the error  $\varepsilon_1$  of the obtained Arrhenius dependence in the case of its extrapolation to a wider temperature interval  $(T_1 - \Delta_1, T_2 + \Delta_2)$  ( $\Delta_1 \geq 0, \Delta_2 \geq 0$ ). It may be expressed as

$$\varepsilon_1 / \varepsilon = (T_2 - T_1 + \Delta_1 + \Delta_2) / (T_2 - T_1).$$

It is easy to extend these estimates to a two-stage process since in that case the parameters are determined by separating the stages.

**Examples of Application of the IMEF.** *Kinetics of heat-stimulated desorption of oxygen from high-temperature superconducting ceramic samples.* In the experiment, we used an MS-7302 quadrupole mass spectrometer to study thermodesorption of  $O_2$  from high-temperature superconducting (HTSC) ceramic samples with the composition  $YBa_2Cu_3O_{6.9 \pm 0.1}$  obtained by the SHS technique [7]. The temperature was changed linearly from 300 to 800°C at a rate of  $w = 3$  deg/min. The thermodesorption curve for oxygen is depicted in Fig. 3a. The first peak pertains to desorption of oxygen of an orthorhombic superconducting phase, and the second one - to a tetragonal phase not exhibiting superconducting properties.

Analysis of the diagnostic curve in Fig. 3b reveals that its initial section (from 350 to 400°C) should be excluded from consideration since diffusion plays a large part here and the model (1) fails to fit the process. In the interval 420-520°C, the process may be considered as consisting of a single stage. On this section, the IMEF may be used to calculate the kinetic parameters and determine the kinetic function. At 520°C, the process becomes more complicated probably because of the influence of the succeeding tetragonal phase. With the parameters and the mechanism of the first stage being found, we may use this portion of the curve to determine the rate constant and the kinetic function of the second stage.

The activation energy of thermodesorption of oxygen of the orthorhombic structure  $E_1$  is found to equal 33,750 cal/mole, and it is determined on the section where  $\lambda(T)$  is stable (from 420 to 460°C, Fig. 3b). Simultaneously with  $\lambda(T)$ , we calculate the function  $k(T)$ . On the interval of stability of  $\lambda(T)$  it gives the value of the preexponential factor. In this case,  $k_1^0 = 2.3 \cdot 10^6 \text{ sec}^{-1}$ . Then the kinetic function is found. On the considered section of the curve it corresponds to a first-order reaction, i.e.,  $f(\eta) = (1 - \eta)$ .

Figure 3c demonstrates how the experimental curve is described by the equation obtained by the IMEF:

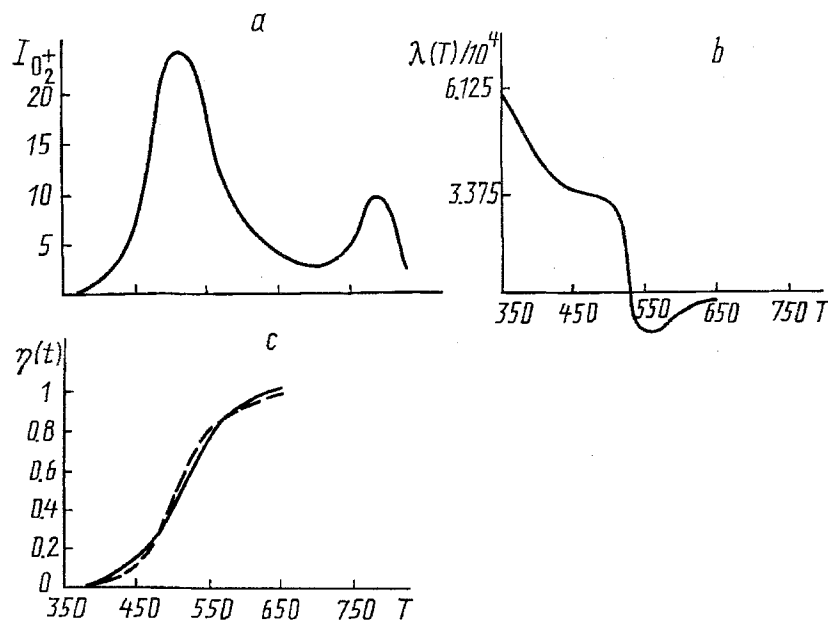


Fig. 3. Oxygen ion current (arbitrary units) (a), diagnostic curve  $\lambda(T)$  (b), experimental (dashed) and calculated curves  $\eta(t)$  (c).

$$\dot{\eta} = 2,3 \cdot 10^6 \exp(-33750/RT)(1 - \eta).$$

As is seen, within the temperature range 420–520°C agreement is very good.

In our case, the accuracy of the experiment is 10–15%, and consequently,  $\epsilon = 0.15$ ,  $T_1 = 420^\circ\text{C}$ ,  $T_2 = 460^\circ\text{C}$ . Hence according to formulas (3), (4),  $\Delta E = 2.9$  kcal/mole,  $\Delta k = 2.2 \cdot 10^6$ , i.e.,  $E = 33.75 \pm 2.9$  kcal/mole,  $k = 2.3 \cdot 10^6 \pm 2.2 \cdot 10^6$  sec<sup>-1</sup>. Thus, the error in determination of  $E$  is no more than 9%, whereas that in determination of  $k$  is  $\approx 96\%$ . But the system is almost insensitive to errors in  $k$  when the order of magnitude is preserved.

If the accuracy to which the kinetic parameters are found is insufficient, one may calculate the optimal conditions of heating at which the error is minimal [4]. Our case does not need this.

*Kinetics and Mechanism of Oxidation of Copper by Barium Peroxide.* We have studied the kinetics and established a mechanism of copper-barium peroxide interaction that provides combustion of the mixture of powder components used for SHS of high-temperature superconducting  $\text{Y}_{123}$ .

The combustion of the mixture and the composition of the end products depend considerably on the external pressure of oxygen. Both at a low partial pressure of oxygen (argon, air) and at  $P_{\text{O}_2} \geq 20$  atm the mixture fails to burn without reheating. Construction of a macrokinetic model of the combustion process may help to explain this phenomenon.

The kinetic experiments were conducted on a complex consisting of a TAG 24-5-24 thermoanalyzer (Setaram, France) and an IBM PC.

Analysis of the end products of the mixture showed that in the presence of external oxygen the high-temperature and low-temperature mechanisms of oxidation of copper are different. It is established (the DTA experiment in air) that up to the melting point of  $\text{BaO}_2$  ( $T \approx 380^\circ\text{C}$ ) copper is oxidized by the external oxygen. Mathematical processing of thermoanalytical curves recorded at a slow rate of heating (5 deg/min) revealed the presence of the both oxidation mechanisms (up to  $T = 380^\circ$  the process is characterized by some kinetic parameters, then - substantially by others). In a combustion regime, high-temperature heating is realized ( $\approx 500^\circ\text{C}$ ), and therefore low-temperature processes may be neglected. Without the external oxygen (argon atmosphere), no low-temperature oxidation mechanism exists. Upon slow heating, the same end products as in the combustion process were obtained. This has dictated the choice of the mechanism used as a basis for constructing the macrokinetic

model. Quantitative kinetic analysis of the DTA curves has allowed us to describe combustion as a gross single-stage process with an activation energy of 17 kcal/mole.

## NOTATION

T, temperature; C, specific heat;  $\rho$ , density,  $\alpha$ , heat transfer coefficient; S, V, surface and volume of the reaction vessel;  $\eta$ , degree of transformation; E, activation energy;  $k^0$ , preexponential factor; R, gas constant;  $f(\eta)$ , kinetic function;  $\dot{q}$ , rate of heat release; Q, thermal effect of the reaction;  $q(t)$ , amount of released heat;  $\lambda$ , zeroth-order approximation for the activation energy;  $\varepsilon$ , relative error.

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