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.

Researchers 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.


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:

\[
C_p \dot{T} = \dot{q} - \alpha \frac{S}{V} (T - T_c), \quad \dot{\eta} = k^0 \exp \left( -\frac{E}{RT} \right) f(\eta), \quad T(0) = T_c, \quad \eta(0) = 0.
\]  

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 \( \dot{q}(t) = C_p \dot{T} + \alpha \frac{S}{V} (T - T_c) \). We will assume that \( C_p \) and \( \frac{S}{V} \) 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 \( Q(\eta) = q(\tau) = \int_0^\tau \dot{q}(\tau) \, d\tau \), 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):

\[
\eta(t) = k^0 \int_{t_0}^t \exp \left( -\frac{E}{RT} (\tau) \right) f(\tau) \, d\tau.
\]