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METHODOLOGICAL PRINCIPLES IN STUDYING CHEMICAL REACTION KINETICS UNDER CONDITIONS OF PROGRAMMED HEATING

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ABSTRACT

The paper describes the methodology of the study of chemical kinetics under non-isothermal conditions realized at programmed heating. A short critical review is given of the available approaches to determine kinetic parameters from thermal analysis data. In order to find thermophysical conditions for a quantitative experiment, the results of a theoretical solution of the problem on the course of a chemical reaction at linear heating are given. An appropriate equipment and methodical ways which provide these conditions are described. For obvious single-stage reactions, the scheme without a priori recalculation of non-isothermal data for isothermal conditions is considered comprehensively, which makes it possible to obtain a kinetic law in a graphic (or parametric) form analogous to that obtained in the isothermal experiment. The aspects of the use of non-isothermal methods for studying the kinetics of complex (multistage) chemical reactions is discussed.

I. INTRODUCTION

Programmed heating is used in a number of popular investigation methods, such as thermography, thermogravimetry, scanning calorimetry, etc.

The interest in various non-isothermal methods of studying chemical reaction kinetics and particularly in the methods related to linear heating has increased recently. First of all, this is caused by a need of kinetic data for fast reactions which occur mostly at high temperatures. These data are necessary for a number of applied and scientific problems. However, their acquisition by traditional isothermal methods is connected with fundamental difficulties.

Firstly, this is true for an effect of substance transformation on heating to the experimental temperature. Inasmuch as with increasing temperature the complete reaction time becomes commensurable with time of heating-up, substance transformation during the heating-up period starts introducing a large error into the appropriate measurements. Secondly, as the ambient temperature (T_0) of the substance under investigation grows, its own temperature may considerably differ from T_0 throughout the whole process. (First of all, this refers to reactions with high values of thermal effect, viz., endothermic and exothermic). This leads to uncertainty in the kinetic experiment, since it is not clear to which temperature the reaction rate should be attributed. Besides, in the case of an exothermic reaction, the process may pass into regimes with uncontrolled development of large self-heatings in the substance up to initiation of thermal explosion or ignition[1].

Application of non-isothermal methods takes these difficulties away to a large degree, as dynamics of changes in temperature and transformation degree is taken into consideration and can be quantitatively taken into account. Rapidness of the experimental procedure and possible usage of a wide temperature range are significant advantages of these methods.

Another important virtue of non-isothermal methods is possible acquisition in some cases (for example, when studying stage reactions) of more complete kinetic information[2]. Finally, significant though not fundamental is the availability of commercial products, and hence rather wide distribution of various devices for thermal analysis, as well as a relative simplicity of a number of sets which can be used for studying the kinetics by other non-isothermal methods. There are various non-isothermal processes[2] (thermal explosion, ignition, propagation of flame, linear pyrolysis, adiabatic compression, programmed heating and other) with which the non-isothermal methods of studying chemical reaction kinetics are created and developed. The present paper is concerned only with the methods related to programmed heating. However, for the continuity of description, it is necessary, first to mention briefly some general problems relating to the majority of non-isothermal methods.

As regards the amount of kinetic information to be obtained, non-isothermal methods may be divided into two groups according to a way of registration, viz., methods with discrete and continuous registrations. Discrete registration is used in methods based on ignition, combustion, linear pyrolysis, adiabatic compression, i.e., particular characteristics of the process under investigation such as ignition delay time, induction period or critical temperature of thermal explosion, rate of combustion or pyrolysis, etc. are measured. When processing experimental data, algebraic expressions are used which are obtained in the theory of these processes and which relate discrete characteristics to parameters defining the process development (heat exchange coefficient, ambient temperature, initial temperature, geometrical, thermophysical, kinetic parameters, etc.). These expressions are plotted in coordinates corresponding to the available formulas, and kinetic parameters are found from the plots.

As a rule, relations between characteristics and parameters of the processes are obtained from the theory for the simplest thermophysical situations and kinetic laws. The main difficulty therefore consists in a correct selection of a theoretical scheme which accurately describes the given process, and in an experimental set-up under distinct controlled conditions corresponding to the scheme chosen. This requires thorough knowledge of the peculiarities of the process, which is a complicated factor.

A rather significant limitation of these methods is also the fact that they do not permit the form of a reaction kinetic law to be found by some predetermined way. A form of kinetic law is preset a priori making use of one or another theoretical formula.

Straightening of experimental data by a scheme chosen at random or from some other considerations is often thought to be a criterion of correctness of the result. This is essentially the main defectiveness of discrete methods of non-isothermal kinetics.

It should be noted that the above-mentioned disadvantages are inherent in a number of schemes used for processing the data obtained by methods of thermographic and thermogravimetric types. This is true for the schemes where use is made not of the whole curve, but of its peculiar points, such as a deviation peak, maximum of reaction rate, furnace temperature corresponding to these points, etc.

Schemes of experimental data processing supported by continuous recording of the quantities measured (and among these are all the methods related to programmed heating) give considerably more complete kinetic information and in principle permit a kinetic law to be found without any a priori assumptions of its form.

It should be noted that such methods as thermography, thermogravimetry, scanning calorimetry, volumetry, etc. were intended for various purposes, and primarily for a qualitative physicochemical analysis. Only recently have they come into use for studying chemical kinetics. Therefore, in most cases industrial designs of devices do not satisfy the aim of their usage for a quantitative kinetic experiment. This primarily concerns the creation of distinct controlled thermophysical conditions in a reaction cell so that the process should be correctly described from the viewpoint of mathematics. Nevertheless, this is very often neglected and it is supposed that a quantitative character of the experimental procedure can be provided by a simple decrease in the heating rate and in the size of weighted amount. As is seen from the thorough consideration, these measures do not often lead to a desirable result.

A solution of a direct problem on the course of some non-isothermal process is always a basis for development and substantiation of various schemes for determining kinetic parameters from the experimental data obtained when studying this process.

One of the problems for the methods of a thermographic type is that of programmed heating where one or another chemical transformation takes place. There exist quite a number of papers in which this problem is solved under different assumptions. Correctness of the methods and schemes used to obtain kinetic data primarily depends on the validity of these assumptions.

The available papers can be divided into three groups depending on the approaches used there.

The solution of the problem on linear heating with the help of the kinetic equation alone is most popular. One non-isothermal factor is taken into account, viz., a preset temperature growth with time, by substituting the appropriate linear temperature dependence on time directly into the kinetic equation (see papers by Murray and White[3], Kissenger[4] and many others).

Popularity of the schemes based on such an approach can be explained by their mathematical simplicity. Their main disadvantage consists in the fact that self-heating* of the system, i.e., the factor which directly affects the rate of the chemical reaction, is completely neglected. It is natural that such an approach cannot take into account the specific character of exo- and endothermic reactions and the influence of parameters defining the heat exchange (heat emission coefficient, heating rate, heat of reaction, size of weighted amount, etc.) on correctness of the method for determining the kinetic data. Purely experimental evaluations are possible, yet they have their own difficulties.

It should be said that sometimes a priori evaluations are made of the size of weighted amount necessary for self-heating to be absent, of the heating rate and of other initial parameters from purely thermophysical positions without taking into account the heat of a chemical reaction. The quasi-stationary lag of temperature is calculated and the conditions are chosen when it is small. It is evident that such evaluations are possible in a limited region of parameters, in particular at small thermal effects which give no significant self-heatings. In a general case, self-heatings may exceed by many fold or even by orders of magnitude a quasi-stationary temperature drop.

A question is sometimes discussed whether it is in general necessary to know the conditions of heat exchange if the measurement schemes used are not connected directly with self-heating and do not require knowledge of heat exchange characteristics for the determination of the reaction rate (for instance, thermogravimetry or scanning calorimetry). It is natural that in this case the conditions of heat exchange are not required for calculation or direct measurement of the reaction rate. However, information on the heat exchange conditions is necessary to know definitely to which temperature the determined rate should be attributed. In this case, for correct quantitative use of experimental data, it is necessary to provide temperature uniformity over the reaction volume and to measure the temperature of the substance under investigation. Complete elimination of self-heating is not necessary and is needed only in the case when temperature uniformity is not provided. Appropriate methodical ways for flattening the temperature and decreasing the self-heating are considered below.

The second group includes the papers where the kinetic equation and the equation of thermal balance written under the assumption of temperature uniformity over the reaction volume are considered simultaneously (Borchardt and Daniels[5]; Reed et al.[6]; Merzhanov et al.[7] and others). For the general case, such an approach is significantly better to reality, being strict enough when temperature uniformity is provided in the experiment over the reaction volume by special means. Naturally, it is impossible within the scope of this approach to evaluate the region of parameters

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* Unless otherwise specified, "self-heating" means a change in the temperature of a substance as compared to that of an inert substance. The change depends on the course of the reaction in the substance, being positive for the exothermic and negative for the endothermic reaction.

where temperature distribution is sufficiently uniform. However, comparison with a more general case shows that this region is rather wide. Therefore, the equation of thermal balance considered simultaneously with the kinetic equation is the basis for creation and substantiation of inverse kinetic schemes.

The third group comprises the papers[8, 9] and others where the kinetic equation is considered simultaneously with the equation of thermal conductivity, which permits the most complete description of the process development to be made. Such a description requires rather arduous mathematical calculations even if the diffusive and hydrodynamic factors are neglected. The main assumption of these papers is the acceptance of independence of transformation degree on the space coordinate. Such an assumption leads to a significant flattening of the temperature distribution and hence can affect the dependences of the process characteristics on parameters. In papers[10, 11] the problem is analysed taking into account the spatial distribution of temperature and transformation degree.

II. A THEORETICAL ANALYSIS OF THE PROBLEM ON LINEAR HEATING OF A REACTANT

Solution of the problem taking into account the distribution of temperature T and transformation degree α is important for substantiating a particular assumption and for revealing various effects connected with spatial non-uniformity of the values T and α. Let us consider this problem for the simplest case of a first-order reaction under the assumption of conductive heat transfer over the reactant.

The initial equation system in dimensional variables is
equation of thermal conductivity

$$c\rho \frac{\partial T}{\partial t} = \lambda \left(\frac{\partial^2 T}{\partial x^2} + \frac{n}{x} \frac{\partial T}{\partial x} \right) + Q \frac{\partial \alpha}{\partial t} \quad (1)$$

equation of chemical kinetics

$$\frac{\partial \alpha}{\partial t} = k_0 \exp(-E/RT)(1 - \alpha) \quad (2)$$

initial conditions

$$t = 0,\ T = T_0 = T_i,\ \alpha = 0 \quad (3)$$

boundary conditions

$$x = 0,\ \frac{\partial T}{\partial x} = 0;\ x = r,\ -\lambda \frac{\partial T}{\partial x} = h(T - T_0) \quad (4)$$

conditions for changing the ambient temperature

$$T_0(T_i, t) = T_i + wt \quad (5)$$

Here T_i is initial temperature, T_0 ambient temperature, x coordinate, r characteristic dimension, t time; c, ρ, λ are thermal capacity, density and thermal conductivity, respectively; Q is heat of the reaction (per unit substance volume), k_0 pre-exponential factor, E activation energy, w rate of heating, h heat transfer coefficient, R universal gas constant, n coefficient of a form ($n = 0$ for a rectangular plate, $n = 1$ for an infinite cylinder, $n = 2$ for a ball).

It is convenient to solve the problem in a dimensionless form. A scale temperature T_* and a form of dimensionless parameters are chosen in the same way as in the problem on thermal explosion under the conditions of linear heating[12].

Dimensionless system of equations is of the form

$$\Omega \frac{\partial \theta}{\partial \theta_0} = \frac{1}{\delta^*(\mathrm{Bi})} \left(\frac{\partial^2 \theta}{\partial \xi^2} + \frac{1}{\xi} \frac{\partial \theta}{\partial \xi} \right) + \exp\left(\frac{\theta}{1 + \beta\theta} \right) (1 - \alpha)$$

$$\Omega \frac{\partial \alpha}{\partial \theta_0} = \gamma \exp\left(\frac{\theta}{1 + \beta\theta} \right) (1 - \alpha) \tag{6}$$

$$\theta = \theta_0 = \theta_i;\ \alpha = 0$$

$$\xi = 0, \frac{\partial \theta}{\partial \xi} = 0;\ \xi = 1, \frac{\partial \theta}{\partial \xi} = -\,\mathrm{Bi}(\theta - \theta_0)$$

The dimensionless variables sought are the temperature

$$\theta = \frac{E}{RT_*^2}(T - T_*)$$

and transformation degree α, independent variables are the ambient temperature

$$\theta_0 = \frac{E}{RT_*^2}(T_0 - T_*)$$

and coordinate

$$\xi = \frac{x}{r}.$$

Dimensionless parameters

$$\Omega = \frac{c\rho w}{Qk_0 \exp(-E/RT_*)}$$

rate,

$$\theta_i = \frac{E}{RT_*^2}(T_i - T_*)$$

initial temperature,

$$\mathrm{Bi} = \frac{hr}{\lambda}$$

Bio criterion characteristic of the heat exchange with the environment;

$$\gamma = \frac{c\rho RT_*^2}{QE}, \beta = \frac{RT_*}{E}$$

are kinetic parameters.

$$\delta^*(\mathrm{Bi}) = \frac{Qk_0Er^2 \exp\left(-E/RT_*\right)}{\lambda RT_*^2}$$

$$= \frac{\delta_n^* \mathrm{Bi}}{2}\left(\sqrt{B_i^2 + 4} - B_i\right) \exp \frac{\sqrt{\mathrm{Bi}^2 + 4} - \mathrm{Bi} - 2}{\mathrm{Bi}} \qquad (7)$$

where δ_n^* is the critical value of the Frank–Kamenetsky criterion[13] for the classical problem on thermal explosion at $\mathrm{Bi} = \infty$ for the reaction of zero order ($\delta_0^* = 0.88$; $\delta_1^* = 2$; $\delta_2^* = 3.32$).

Expression (7) is obtained from the solution of a boundary value problem on thermal explosion[14]. In the equation system (6) δ^* is not a parameter, since its numerical value can be calculated for concrete geometry at known conditions for heat exchange. This value is used for calculating the scale temperature T_* from eqn. (7). For exothermic reactions the temperature T_* has a distinct physical sense, viz., it is a critical temperature of thermal explosion under static ($T_0 = \mathrm{const.}$) conditions. For convenience, the definition of T_* is retained when considering an endothermic reaction.

The physical sense of the basic parameter Ω becomes clear after simple transformations of the expression for quasi-stationary lag ΔT_q of the central temperature with respect to the surface under the steady regime without taking into account the reaction

$$\Delta T_q = -\frac{wr^2}{2(n + 1)a} \qquad (8)$$

where

$$a = \frac{\lambda}{c\rho}$$

is a thermal diffusivity coefficient. In the dimensionless form

$$\Omega = -A\frac{\Delta T_q}{\Delta T_*} = -A\Delta\theta_q \qquad (9)$$

where

$$A = \frac{2(n + 1)}{\delta^*(\mathrm{Bi})}$$

(for instance, at $n = 1$, $\mathrm{Bi} = \infty$, $A = 2$);

$$\Delta T_* = \frac{RT_*^2}{E}$$

is the "Semenov" characteristic temperature interval. Thus with an accuracy of a constant, Ω is a dimensionless quasi-stationary temperature drop between the surface and the centre.

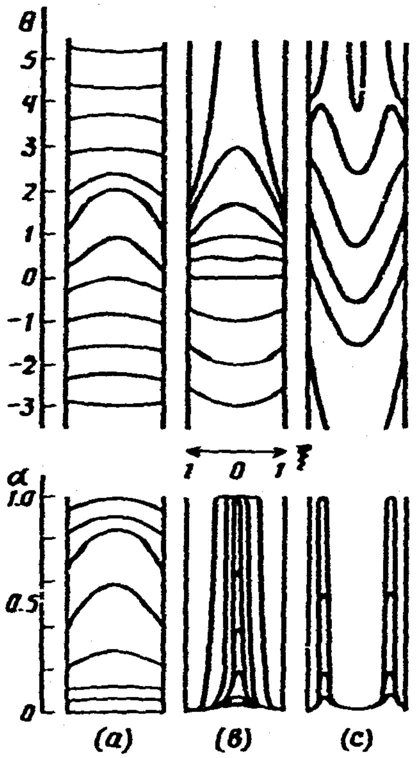
Parameter γ is the relation between scale times of adiabatic and isothermal reactions. Exo- and endothermic effects become less as γ increase. Increase of parameter γ can be experimentally realized by dilution of a reactant with an inert substance. Parameter β is characteristic of a relative steepness of an Arrhenius exponent. The solution was carried out by a numerical method for a cylindrical form ($n = 1$) over a wide range of changes in parameters Ω, γ, β, Bi. This solution has permitted a number of qualitative effects to be established, part of which is a direct consequence of temperature non-uniformity. Dependence of the characteristics on θ_i was not investigated; in all calculations θ_i was chosen so that a quasi-stationary thermal regime could be retained by the start of marked heat release. In addition to distributions of temperature and transformation degree, various process characteristics were determined in the solution, viz., peak of temperature deviation, maximum of the reaction rate in the centre, maximum of the heat flow through the surface, ambient temperatures corresponding to these extremums, characteristics averaged over coordinate, etc.

The characteristic property of the process development for highly exothermic reactions is a sharp change of regimes at changes in the rate Ω (Fig. 1). At small Ω negligible self-heatings occur; thermal explosion takes place beginning with some critical Ω_*; at considerable increase in Ω there occurs a transition to ignition starting at the substance surface. Thermal explosion under dynamic conditions is a well-studied phenomenon, and there exists the quasi-stationary theory by Merzhanov and co-workers[15-17, 12] which permits its characteristics to be calculated.

Thermal explosion is the undesirable regime for a kinetic investigation as it practically excludes a possibility of continuous recording of the process.

Theoretical calculations consistent with the experimental data on the critical conditions of thermal explosion under the dynamic conditions[18, 19] make it possible to conclude that even with small weighted amounts usually used in thermal analysis, critical rates for many explosives are rather small. As an example, we shall give the results of theoretical calculation of the critical rate for a cylindrical pellet of pyroxyline ($Q = 1125$ cal g^{-1}; $E = 48.5$ cal mol^{-1}, $k_0 = 3.76 \cdot 10^{18}$ sec^{-1}; $c = 0.31$ cal g^{-1} deg^{-1}; $\rho = 1.5$ g cm^{-3}; $\lambda = 3 \cdot 10^{-4}$ cal cm^{-1} sec^{-1} deg^{-1}) of 0.1 g by weight. The calculations show that $\Omega_* = 0.033$, which corresponds to the dimensional critical rate $w_* = 0.7$ deg min^{-1}. Thus, even a small weighted amount of pyroxyline will spontaneously ignite practically at all heating rates of the devices produced (0.1 to 100 deg min^{-1}).

Figure 2 shows a dependence of maximum deviation in the centre of reaction volume on the dimensionless rate Ω. At small γ, a form of this dependence is of an



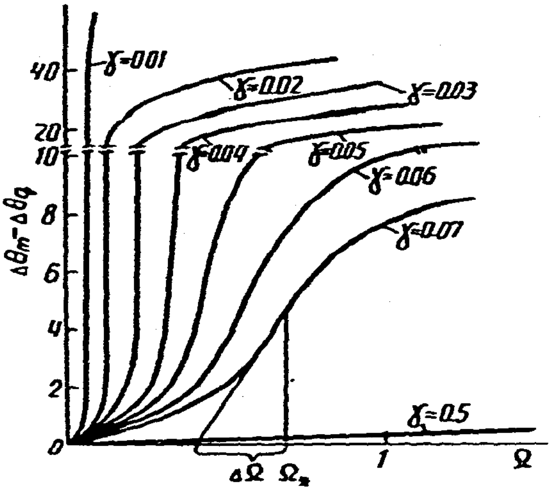


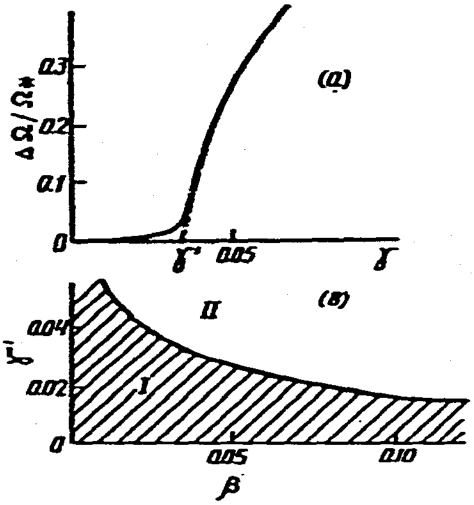
Fig. 1. Distribution of temperature and transformation degree (exothermic reaction). $\gamma = 0.005$; $\beta = 0.03$; $Bi = \infty$.
(a) $\Omega = 0.025$; (b) $\Omega = 1$; (c) $\Omega = 5$.

Fig. 2. Dependence of the peak temperature deviation at the centre on the heating rate (exothermic reaction) $Bi = \infty$. γ = var.

explosive character. With increasing γ, the dependence becomes more and more smooth, and the deviations become progressively less. When describing the region of transition from small to great heatings by the relation of $\Delta\Omega$ to Ω, corresponding to the inflection point and clear from the figure, one can conditionally (as is done for the static conditions[20]) separate the normal regimes of thermal explosion where this value is negligibly small and those degenerated where it is appreciable.

Figure 3 illustrates the way of determining the interface γ' of normal and degenerated regimes of thermal explosion, and shows the dependence γ' (β). It should be noted that a form of the function γ' ‘β) is practically independent of criterion Bi. Further increase of γ leads to complete degeneration of thermal explosion, which is characterized by the absence of the S-form in the curves of dependence of deviation spikes on the heating rate.

In the region of complete degeneration the picture of the process development changes qualitatively (Fig. 4). The curves of distribution of temperature and transformation degree remain concave throughout the process, since the heat in the system is not sufficiently high to compensate the initial quasi-stationary drop.



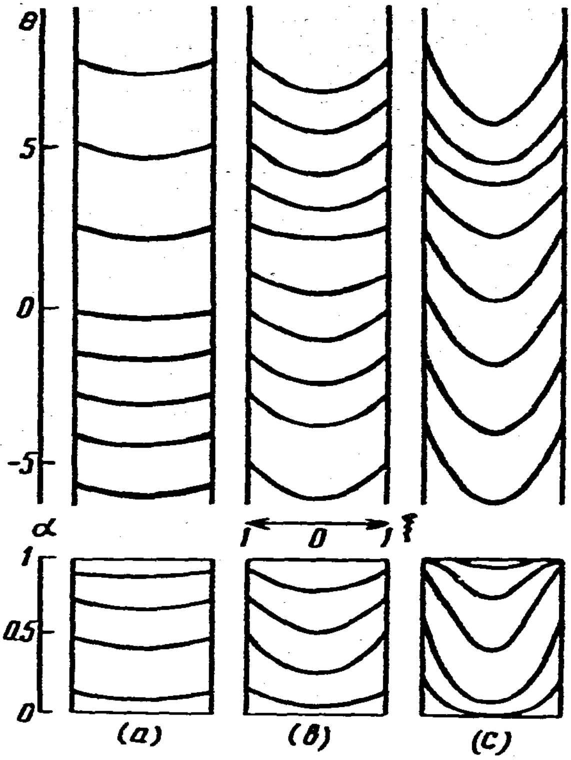


Fig. 3. Degeneration of thermal explosion.
(a) Method of determining γ' ($\beta = 0.03$; Bi $= \infty$). (b) Dependence $\gamma'(\beta)$. I = region of normal regimes of thermal explosion; II = region of degenerated regimes.

Fig. 4. Distribution of temperature and transformation degree in the region of strong degeneration (exothermic reaction). $\gamma = 0.5$; $\beta = 0.03$; Bi $= \infty$.
(a) $\Omega = 0.6$; (b) $\Omega = 2$; (c) $\Omega = 5$.

When studying the kinetics of chemical reactions, evaluation of temperature non-uniformity over the reaction volume is of special importance. As noted above, calculation by eqn (8) obtained without taking account of the chemical reaction may lead to a considerable error. Figure 5 shows the relation of maximum temperature difference between the centre and the surface to a quasi-stationary lag determined from eqn (9) depending on γ. It can be seen from the figure that at small γ (a strong exothermic effect), this relation is very large. The dependence given slightly depends on Bi and β throughout the region of the parameters. At $\Omega < \Omega_*$, as well as in the region of strong degeneration ($\gamma \gg \gamma^1$) the relation $\Delta\theta_m/|\Delta\theta_q|$ slightly depends on Ω. This permits the region of values of γ to be pointed where temperature non-uniformity can be evaluated by eqn (8). It is seen from Fig. 5 that $(\Delta\theta_m/|\Delta\theta_q|) \leqslant 1$ at $\gamma \geqslant 0.21$, i.e., the temperature difference between the centre and the surface does not exceed $|\Delta\theta_q|$ upon heating.

It should be noted that temperature non-uniformity can be evaluated approximately using the quasi-stationary theory of thermal explosion[15–17] under the

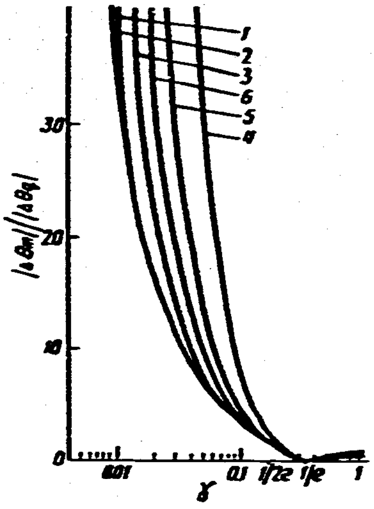


Fig. 5. Ratio of the maximum temperature difference between the centre and the surface to quasi-stationary lag depending on (exothermic reaction). Bi $= \infty$; $\beta = 0.03$.
(1) $\Omega = 0.005$; (2) $\Omega = 0.01$; (3) $\Omega = 0.1$; (4) $\Omega = 1$; (5) $= 3$; (6) $\Omega = 5$.

assumption of temperature uniformity over the reaction volume. Taking into account the temperature distribution similar to that in papers[12, 15-17], we shall obtain the expression for a critical heating rate

$$\Omega_* = \frac{2e(n+1)\gamma\,\mathrm{Bi}}{\delta^*(\mathrm{Bi})(1-e\gamma)(\mathrm{Bi}+2)} \tag{10}$$

maximum temperature difference between the centre and the surface

$$\Delta\theta_m = \frac{\delta^*(\mathrm{Bi})(1-e\gamma)\Omega}{2e(n+1)\gamma} \tag{11}$$

and the ambient temperature corresponding to $\Delta\theta_m$

$$\theta_{om} = \ln\frac{\Omega}{\gamma} + \frac{\delta^*(\mathrm{Bi})(e\gamma-1)(\mathrm{Bi}+2)\Omega}{2e(n+1)\gamma\,\mathrm{Bi}} \tag{12}$$

When $\Omega < \Omega_*$ eqn (11) is valid with an accuracy of about 20 to 30% throughout the interval of γ and Bi. If $\Omega > \Omega_*$ eqn (11) can be used for evaluating by an order of value.

Substituting (9) into (11), we obtain

$$\frac{\Delta\theta_m}{|\Delta\theta_q|} = \frac{1-e\gamma}{e\gamma} \tag{13}$$

From this we shall determine γ^*, equating $\Delta\theta_m/|\Delta\theta_q|$ to a unity in (13)

$$\gamma^* = \frac{1}{2e} = 0.184 \tag{14}$$

which agrees well with numerical count. In addition to γ^*, a value of γ^{**} can be obtained from (13) which is also characteristic of the region of complete degeneration. Starting with this value, heating-up in the system cannot compensate a quasi-stationary lag ($\Delta\theta_m = 0$). It is evident that

$$\gamma^{**} = \frac{1}{e} = 0.368 \tag{15}$$

This value also agrees well with numerical count (Fig. 5).

In the case of endothermic reactions (Fig. 6), no qualitative differences in the process development are observed, either at changes of the rate, or at changes of kinetic parameters γ and β, since the reaction always begins near the surface. Maximum of temperature deviation monotonically grows with increasing rate. When the modulus of parameter γ increases, distribution curves $\theta = \theta(\xi)$, $\alpha = \alpha(\xi)$ and $\dot{\alpha} = \dot{\alpha}(\xi)$ are flattened.

Figure 7 shows the dependence of relation $\Delta\theta_m/\Delta\theta_q$ on the modulus of parameter γ. As in the case of exothermic reactions, parameters B_i and β slightly affect this dependence. Since the profile of temperature in the coordinate is always concave,

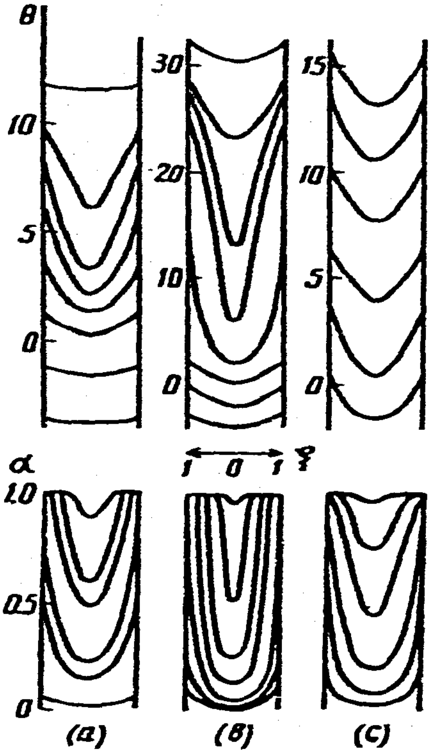


Fig. 6. Distribution of temperature and transformation degree (endothermic reaction, Bi $= \infty$, $\beta = 0.03$).
(a) $\gamma = -0.005$, $\Omega = -0.3$; (b) $\gamma = -0.005$, $\Omega = -3$; (c) $\gamma = -0.5$, $\Omega = -5$.

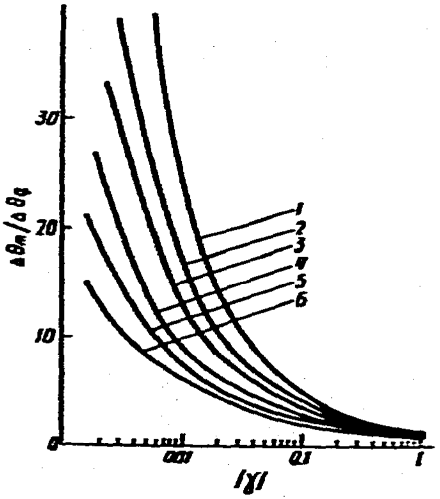


Fig. 7. Ratio of the maximum temperature difference between the centre and the surface to quasi-stationary lag (endothermic reaction) Bi $= \infty$. $\beta = 0.03$.
(1) $\Omega = -0.1$; (2) $\Omega = -0.5$; (3) $\Omega = -1$; (4) $\Omega = -3$; (5) $\Omega = -5$; (6) $\Omega = -10$.

the value $\Delta\theta_m/\Delta\theta_q \rightarrow 1$ with growth of $|\gamma|$ asymptotically. The value of $|\gamma^*| = 1$ may be conditionally specified with an accuracy of 20%, beginning with which non-uniformity of temperature distribution over the reaction volume will be defined by a quasi-stationary lag (eqn 8). For values $|\gamma| < |\gamma^*| = 1$, the formula can be used which is chosen from the results of numerical count over the interval of changes of $|\Omega| = 0.1 \div 10$; $\mathrm{Bi} = 0.002 \div \infty$; $\beta = 0.03$ with an accuracy not worse that 20%

$$\frac{\Delta\theta_m}{\Delta\theta_q} = 0.6 + p\,|\gamma|^{-p} \tag{16}$$

where $p = 0.65 - 0.12 \lg |\Omega|$.

It is quite evident that temperature non-uniformity over the reaction volume leads to an error in the determination of the reaction rate. However, for quantitative evaluations a criterion is needed which relates a permissible temperature difference in the reaction volume and a required accuracy in determining a reaction rate. Let the temperature in the sample be located between values of $T_{\max}$ and $T_{\min}$ at a given moment. Neglecting the difference between $\alpha(T_{\max})$ and $\alpha(T_{\min})$ as compared to the Arrhenius dependence $\dot{\alpha}(T)$ and making use of the Frank–Kamenetsky exponential expansion[13], we obtain the following relation from the kinetic equation

$$\dot{\alpha}(T_{\max}) = \dot{\alpha}(T_{\min}) \exp\left[\frac{E}{RT_{\min}^2}\,(T_{\max} - T_{\min})\right]$$

Performing expansion of an exponential in a series for approximate evaluation and making use of the first two members, we have

$$\frac{\dot{\alpha}(T_{\max}) - \dot{\alpha}(T_{\min})}{\dot{\alpha}(T_{\min})} = \frac{E}{RT_{\min}^2}\,(T_{\max} - T_{\min}) \tag{17}$$

The left-hand side of eqn (17) represents a relative error in determining a reaction rate at the cost of temperature non-uniformity. Maximum error in determining the rate ε corresponds to the maximum temperature difference between the centre and the surface. Hence, the criterion of temperature "uniformity" may be given in the form following from (17)

$$\Delta T_m < \varepsilon \frac{RT_{1\,\min}^2}{E} \tag{18}$$

Here $T_{1\,\min}$ is the minimal temperature within the reaction volume at the moment corresponding to maximum temperature difference. For evaluations, T_* may be used in (18) with a sufficient accuracy instead of $T_{1\,\min}$.

Of interest is the question about mutual arrangement of maximum temperature deviation and maximum reaction rate on thermographic curves. This interest is associated with the fact that coincidence of these maxima is postulated in a number of schemes for determining kinetic parameters. Reed et al.[6] have found that in the absence of temperature distribution, the maximum of the reaction rate is always ahead of the maximum of temperature deviation. A numerical analysis shows that when distribution is available, their mutual arrangement depends on the profile form, and hence on parameters affecting the profile. For exothermic reactions, the profiles are convex under the ignition limits. The sequence of extremes with time is as follows: first, a peak of the rate in the centre, then a peak of deviation, and finally, maximum of the mean rate. (By the way, the mean rate in coordinate is of special interest, since even when distribution, for instance by the thermogravimetrical method, is available, only this rate can be determined.) Under the critical regime and at short distance from it, all the special points practically coincide. Moving away from the limit and passing into the region of degeneration, when profiles become concave, the peak of the mean rate begins to exceed that of temperature deviation, i.e., the reverse picture is observed. In the case of endothermic reactions, when profiles of temperature and transformation degree are concave throughout the process, the maximum of the mean rate always exceeds the maximum of deviation. This is clear, since with convex profile, the transformation of the substance in the centre prevails over the transformation in volume as a whole; with concave profile, the opposite is true.

The analysis of the characteristic features of the process development connected with the availability of temperature and transformation degree distributions, such as change in positions of extremes, formation of ignition regimes, evaluation of temperature drop over the reaction volume, is naturally possible only when solving the problem in its most complete form.

In the general case, the equation of thermal balance refers to a model without temperature distribution over a substance and hence does not basically take into account the effects connected with this distribution. However, the question arises, under which conditions this equation reflects quantitatively correctly macrokinetics of the process as a whole. It is also of interest to know the width of the region of parameters where the process can be described with the help of the kinetic equation without taking account of thermal balance.

To answer these questions, the solution of the equation system, written under the assumption of temperature uniformity over the space, is:

$$\Omega \frac{d\theta}{d\theta_0} = \exp\left(\frac{\theta}{1+\beta\theta}\right)(1-\alpha) - \frac{1}{\varkappa_*}(\theta - \theta_0) \tag{19}$$

$$\Omega \frac{d\alpha}{d\theta_0} = \gamma \exp\left(\frac{\theta}{1+\beta\theta}\right)(1-\alpha)$$

$$\theta = \theta_0 = \theta_i;\ \alpha = 0$$

and of the kinetic equation written without taking account of the heat exchange with the surroundings:

$$\Omega \frac{d\alpha}{d\theta_0} = \gamma \exp\left(\frac{\theta_0}{1+\beta\theta_0}\right)(1-\alpha) \tag{20}$$

$$\theta_0 = \theta_i;\ \alpha = 0$$

has been carried out simultaneously with equation system (6). A scale temperature for system (19) is calculated from the Semenov criterion[21]

$$x_* = \frac{Qk_0EV}{hSRT_*^2} \exp(-E/RT_*) = \frac{1}{e} \tag{21}$$

Here V is volume, S surface, e base of natural logarithms; for the simplest forms $\frac{S}{V} = \frac{n+1}{r}$.

As noted above, system (19) agrees with the experimental conditions where temperature uniformity over the reaction volume is provided by special means. In this case, the coefficient h has a distinct physical meaning of the coefficient of heat transfer from the outer surface of a reactant to the surroundings. When system (19) is used for an approximate description of the process where a conductive transfer over a reactant plays a significant role, it is necessary to present a method for calculating the coefficient h which in this case has the meaning of an efficient value.

Let us use the method proposed by Frank-Kamenetsky[13] and introduce h_{eff} postulating an equality of T_* obtained from (7) and (21)

$$h_{eff} = \frac{e\lambda\delta^*}{(n+1)r} \tag{22}$$

It is convenient to determine h_{eff} from (22) since all the dimensionless parameters where T_* enters become identical for systems (7), (19) and (20).

First, let us consider an exothermic reaction. In the region of a normal thermal explosion, calculation of the criticalc onditions is of the greatest interest for making methodical evaluations. It turns out that due to the appropriate choice of a scale temperature, a dimensionless critical rate Ω_* does not practically depend on the Bio criterion, i.e., evaluation of critical heating rates can be performed from the averaged equation system (19) to a very high accuracy. From the viewpoint of thermographic methods, the region of thermal explosion degeneration is of the greatest interest. Figure 8 gives a comparison of dependence of temperature deviation peak and its position on a dimensionless rate in the region of degeneration. It is interesting that the position of the spike calculated from (6) and (19) coincides with fair accuracy over a wide range of parameters (an error is not more than 15% even at Bi → ∞, i.e., at boundary conditions of the first kind). The difference in the values of the peaks as such is greater. Divergence at $\mathrm{Bi} < 5$ reaches 40% even at low rates. At $\mathrm{Bi} < 1$ agreement of the solutions is quite satisfactory. In Fig. 9 a comparison is given of the maxima of a mean rate and their positions calculated from the three systems (6), (19) and (20). Comparison of the systems (6) and (19) gives a result identical to that mentioned above. As regards the kinetic equation (20), both maximum of the rate and its position obtained from its solution starting from low rates (approximately from $\Omega = 0.1$) differ very greatly from those obtained both from the solution of the averaged system, and from solutions of the system taking account of the distributions.

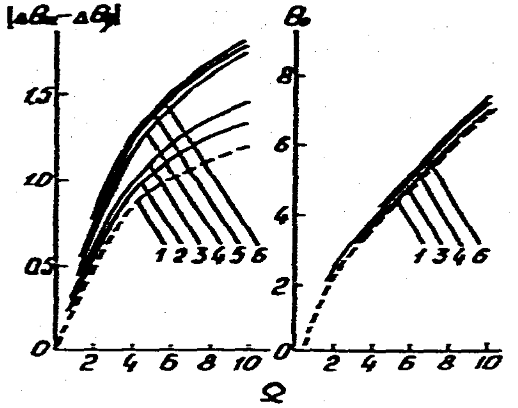


Fig. 8. Dependence of modules of the temperature deviation peak and its position on Ω (exothermic reaction) $\beta = 0.03$; $\gamma = 0.5$.
(1) curves obtained on solution of system (19). (2) Bi = 0.5; (3) Bi = 1; (4) Bi = 5; (5) Bi = 10; (6) Bi = ∞

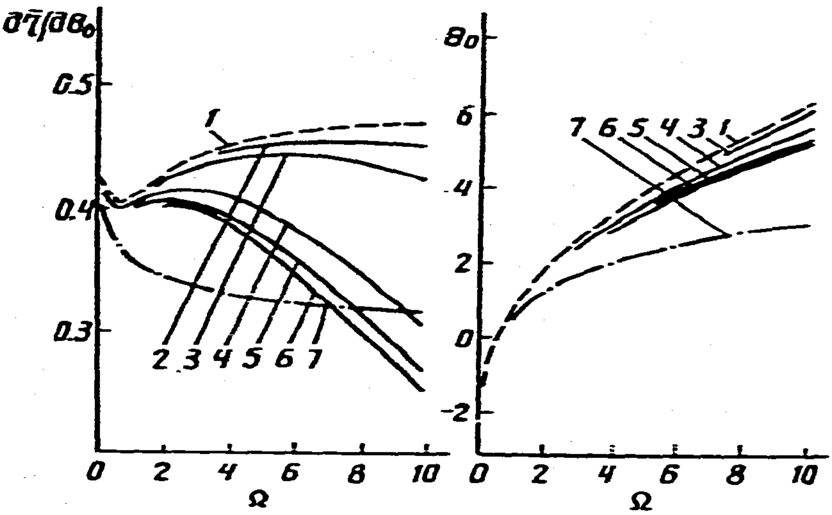


Fig. 9. Dependence of maximum of the mean rate and its position on Ω (exothermic reaction, $\beta = 0.03$; $\gamma = 0.5$).
(1) curves obtained on solution of system (19); (2) Bi = 0.5; (3) Bi = 1; (4) Bi = 5; (5) Bi = 10; (6) Bi = ∞; (7) curves obtained from eqn (20).

Naturally, it is impossible in principle to evaluate either a critical rate or temperature deviation from the kinetic equation. An endothermic reaction has some specific features. The maximum value (Fig. 10) of the mean rate can be calculated from an averaged system with a better accuracy than deviation, and conversely the position (Fig. 11) is better calculated for deviation. Calculations by the kinetic equation give a considerable error, as in the case of the exothermic reaction. As for the exothermic reaction, under the conditions of weak heat exchange a good agreement is observed between the results of solutions of the equation systems solved with and without taking account of temperature and transformation degree distribution.

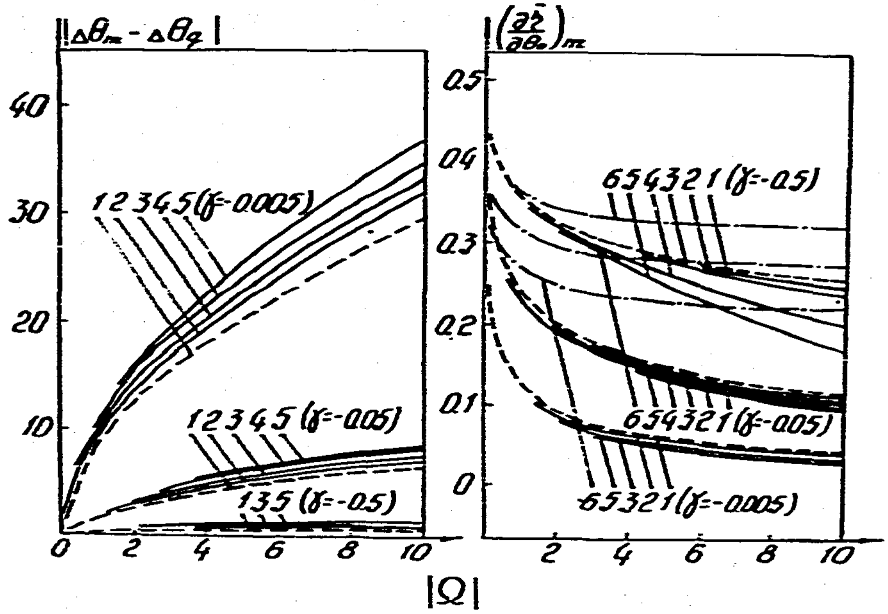


Fig. 10. Dependence of modulus of the temperature deviation peak and maximum of the mean rate on $|\Omega|$ (endothermic reaction, $\beta = 0.03$).
1 = curves obtained from the results of solution of system (19); (2) Bi = 0.5; (3) Bi = 1; (4) Bi = 5; (5) Bi $= \infty$; (6) curves obtained from eqn (20).

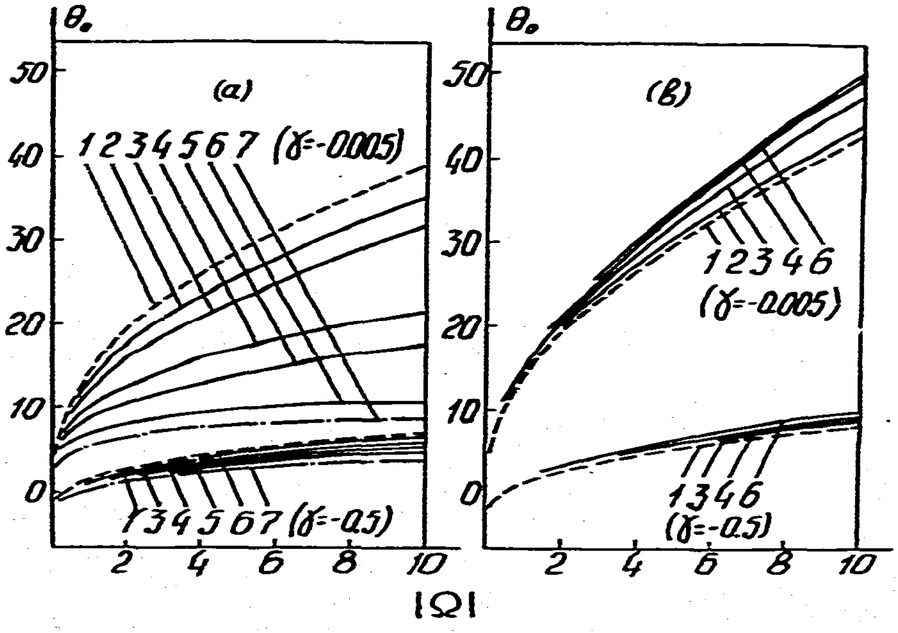


Fig. 11. Dependence on $|\Omega|$ of the positions of mean rate maximum (a) and of temperature deviation peak (b) (endothermic reaction, $\beta = 0.03$).
(1) curves obtained on solution of system (19); (2) Bi = 0.5; (3) Bi = 1; (4) Bi = 5; (5) Bi = 10; (6) Bi $= \infty$; (7) curves obtained from eqn (20).

Summarizing the analysis of the direct problem, it should be noted that as a whole the equation system (19) with an averaging of temperature and transformation degree in the coordinate describes the process adequately also in the case when heat transfer over a substance is limited by thermal conductivity. In the case of weak heat exchange with the environment ($\mathrm{Bi} \leqslant 1$), this description is practically quantitative.

The kinetic equation (20) which does not take into account the heat exchange at all gives a considerable error when determining the process characteristics over the whole region of changes in parameters at $\Omega > 0.1$ both for exothermic and endothermic reactions.

A solution of the direct problem permits the dilution method to be substantiated, i.e., to find the region of parameters where appearance of exo- and endothermic effects is so weakened that a maximum temperature difference between the centre of a reaction volume and its surface becomes commensurable with a quasi-stationary drop. It should be noted that evaluations of non-uniformity of the temperature field based on the solution of a direct problem require a knowledge of kinetic parameters of a reactant and in principle cannot be used a priori for the experiment on studying chemical kinetics. In many cases it is very useful to make preliminary evaluations with the use of reference data on the kinetics of reactions close to those under investigation. However, the solutions obtained from the direct problem can be used most specifically for calculations on substantiation of correctness of an already performed experiment.

III. ON SOLUTION OF THE INVERSE PROBLEM OF NON-ISOTHERMAL KINETICS

In the previous chapter a consideration has been given of the solution of the direct problem on linear heating of a reactant where a form of the kinetic law is preset and under known geometrical, thermophysical and other conditions, the space–time distributions of temperature and transformation degree of a reactant and various process characteristics are found. The analysis of the solution of the direct problem gives useful information on the process and makes it possible to solve a number of methodical questions. However, for non-isothermal kinetics the main problem is an inverse problem which consists in finding a kinetic law from the experimentally obtained form of distributions of temperature, transformation degree, thermal flow, etc.

A great number of inverse kinetic schemes for treating the experimental data obtained by the methods of thermal analysis exists at present (see reviews[2, 22–24] and the monograph[8]). The problem is considered most comprehensively for gross single-stage reactions, i.e., for the case when the process may be described by the kinetic equation of the following type

$$\dot{\alpha} = \dot{\alpha}(T, \alpha) \tag{23}$$

as a rule, being assumed to be

$$\dot{\alpha}(T, \alpha) = k(T) \cdot f(\alpha) \tag{24}$$

Recently a discussion has arisen whether it is justified to use an equation of type (23) for describing non-isothermal processes or (in a somewhat different statement of the problem) identity of the kinetic equations obtained by isothermal and non-isothermal methods. This discussion has two aspects. The first, a formally mathematical[25] incorrectly assumes that in non-isothermal processes the time t and temperature T are independent variables. On the basis of incorrect mathematical operations of partial differentiation it is stated[25] that equations of type (23) or (24) cannot be used for the description of a non-isothermal process. Incorrectness of this concept has been convincingly shown[26-28].

The second aspect of the discussion is the uncertainty as to possible use of eqn (23) for describing non-isothermal processes due to the fact that it is obtained under the assumption of evenly balanced Maxwell–Boltzmann distribution of energies of reacting molecules according to the degree of freedom (for instance, see ref. 26). This question is set in principle correctly. If a rate of the process, disturbing an equilibrium distribution (for programmed heating, this is a preset rate of the temperature growth), is greater or proportionate with a rate of the slowest relaxation processes, then naturally, eqn (23) loses its sense, since the concept of "temperature" as such loses its sense.

However, the characteristic times of establishing equilibria according to the internal degree of freedom are usually much less than the characteristic times of heating. Thus, one of the slowest relaxation processes is an oscillatory relaxation for gaseous systems ($t_{rel} \sim 10^{-4} \div 10^{-6}$ sec). The upper boundary of the heating rate corresponding to these relaxation times $w \sim 10^{7} \div 10^{9}$ deg sec^{-1} lies many orders higher than the heating rates used in thermal analysis. The factor which disturbs the equilibrium may be a chemical reaction itself[29], if a characteristic time of reaction is commensurable or less than relaxation time. However, a specific character of the course of the non-isothermal process is not of a decisive importance here.

As in reviews[22-24] a thorough description is given of the concrete schemes for obtaining kinetic parameters from non-isothermal data, we shall confine ourselves here to critical discussion of some general statements of the investigations considered in these reviews. In most of the schemes proposed the experimental data are treated with the help of the equations of type (23) and (24) taking into account a programmed growth of temperature $T(t)$ but without considering the heat balance with the environment. It was shown in the preceding part for the first-order reaction that in this case the process is described with an error significantly growing with increase in the heating rate and intensification of an exo- or endothermic effect of the reaction. It is rather difficult to take into account all the errors resulting from this thermophysical fact. A scheme correct as regards the thermophysical aspect for performing the experiment and processing the data obtained is realized in papers by Borchardt and Daniels[5] and Reed et al.[6]. In these papers the heat exchange with the environment is taken into account with the help of the equation of heat balance.

A general methodological disadvantage of most schemes proposed, among them the schemes of papers[5, 6], is a priori presetting of the form of the kinetic function

$f(\alpha)$. Making use of the experimental data either for determining characteristics in extreme points at various heating rates (for instance, in the method by Kissinger the environmental temperature is determined at the maximum reaction rate) or for determining a non-isothermal reaction rate at different moments of the process, the experimental data are plotted in co-ordinates following from the kinetic equation, and then kinetic parameters are found by mathematical methods.

A disadvantage of this procedure, besides presetting a form of $f(\alpha)$, is the fact that due to a strong Arrhenius dependence of the reaction rate on temperature; the straightening slightly depends on the form of function $f(\alpha)$ and therefore determination of its parameters (even if the form of function is preset correctly) is not well-founded.

In papers by Merzhanov, Abramov, Abramova, Shteinberg, Goncharov and others[2, 7, 30, 32] the schemes for processing the experimental data are proposed and used for studying kinetics of chemical reactions by the non-isothermal method. The schemes permit a kinetic law to be obtained in the same form (graphical or tabulated) as from the isothermal experiment without a priori assumptions. In fact, this is a way of recalculating the data of non-isothermal experiments for isothermal conditions, which is free of errors possible when postulating a form of function $f(\alpha)$. Let us consider in more detail this method which is applicable with small modifications to the treatment of thermographical, thermogravimetrical and calorimetric data.

For certainty, let us first consider the case of DTA. If an experiment is performed with a high degree of dilution of a reactant by an inert substance (description of the appropriate methodical ways is given in the following chapter), then a differential thermogram can be described approximately (with an accuracy of 1–2%) by the following equation system

$$MC\Delta\dot{T} = mQ\dot{\alpha} - h(T)S\Delta T \tag{25}$$

$$\dot{\alpha} = \dot{\alpha}(T, \alpha) \tag{26}$$

$$t = 0, \Delta T = 0, \alpha = 0 \tag{27}$$

Here M and C are total mass and thermal capacity of the cell and inert substance, respectively; m is mass of the substance under investigation, Q heat of the reaction (per unit mass), $h(T)$ heat transfer coefficient taking account of the temperature dependence, S surface of an ampoule, ΔT temperature difference between a cell-"reactor" and a cell-"witness".

Taking experimental measurements of the signal of DTA $\Delta T = \Delta T(w, t)$ and of the standard temperature $T_s = T_s(w, t)$, knowing initial masses of the standard and weighted amount M and, standard heat capacity C, having determined the complex characteristic of the heat exchange between the cell and the furnace

$$h(T)S = \frac{MCw}{\Delta T_s^1(T)}$$

from the preliminary calibrating experiments of lag $\Delta T_s'(T)$ of the temperature of the cell with an inert substance from the temperature of the furnace wall in the region of linear heating with the rate w, and performing the differentiation with respect to time of the signal $\Delta T(w, t)$, the thermal effect Q and kinetic law $\dot{\alpha}(T, \alpha)$ can be found making use of the equation system obtained from (25–27)

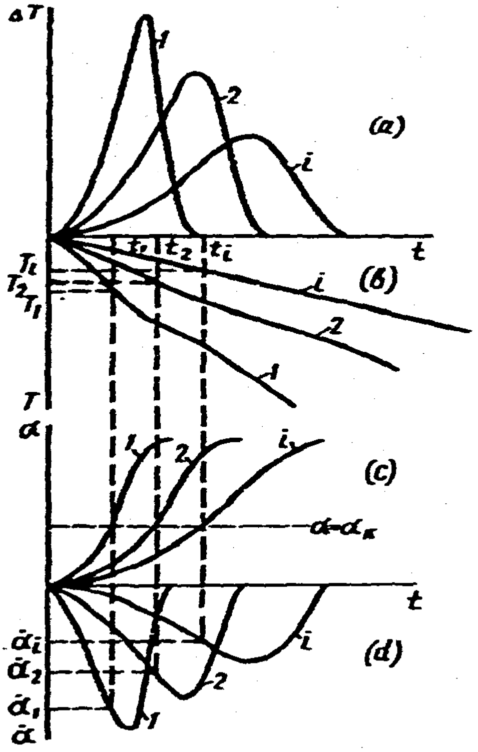
$$Q = \frac{1}{m} \int_0^\infty h(T) S \Delta T dt \tag{28}$$

$$\alpha = \alpha(w, t) = \frac{1}{Qm} \left[MC\Delta T + S \int_0^t h(T) \Delta T dt \right] \tag{29}$$

$$\dot{\alpha} = \dot{\alpha}(w, t) = \frac{1}{Qm} [MC\Delta\dot{T} + h(T) S \Delta T] \tag{30}$$

As the relation $T = T_s + \Delta T = T(w, t)$ is known, expressions (29) and (30) are in fact a parametric form of the kinetic equation record. Actually, excluding w and t from them, we obtain the dependence sought $\dot{\alpha} = \dot{\alpha}(T, \alpha)$. Let us illustrate graphically the procedure described. Let the curves of changing of signal DTA with time $\Delta T = \Delta T(w, t)$ (Fig. 12a) and the plots of changed temperature in the operating cell $T = T(w, t)$ corresponding to these curves (Fig. 12b) be experimentally obtained at several rates of linear heating w_1, w_2, w_i. Having processed the data of Fig. 12a by formulas (29) and (30) the plots of changes in the conversion degree and rate $\alpha = \alpha(w, t)$, $\dot{\alpha} = \dot{\alpha}(w, t)$ can be constructed (Fig. 12c, d), which correspond to the same heating rates w_i. Drawing a straight line $\alpha = \alpha_k = \text{const}$ on the plot, we obtain i points with abscissas t_1, t_2, t_i. One point of T_i (Fig. 12b) and $\dot{\alpha}_i$ (Fig. 12d) corresponds to each moment of t_i. Thus, each value of i in co-ordinates $\dot{\alpha} - T$ gives points whose geometrical position forms a dependence curve $\dot{\alpha}(T)$. To each value of α_1, α_2, α_k there corresponds its own curve $\dot{\alpha}(T)$ and, hence, we obtain a family of k curves $\dot{\alpha} = \dot{\alpha}(T)$ at $\alpha = \text{const}$. (Fig. 13a) which is a graphical expression of the law $\dot{\alpha} = \dot{\alpha}(T, \alpha)$. The number of experimental points on the curve $\dot{\alpha}(T)$ at $\alpha = \text{const}$. equals the number of experiments i with various heating rates w_i.

For gross single-stage processes, the data of Fig. 13a can be plotted in the Arrhenius anamorphosis on the plot ln $\dot{\alpha}$, $(T\,°\text{K})^{-1}$ at $\alpha = \text{const}$. (Fig. 13*b*). In the last-mentioned case, a possibility arises to widen the interval of determining the kinetic law $\dot{\alpha} = \dot{\alpha}(T, \alpha)$ by extrapolation (shown by the dotted lines). The family of curves shown in Fig. 13a, b can be drawn in another way. Drawing horizontal straight lines at $T = T_j = \text{const}$. in Fig. 12b according to time moments t_j corresponding to intersections, α and $\dot{\alpha}$ can be determined and isothermal plots of j curves $\dot{\alpha} = \dot{\alpha}(\alpha)$ can be drawn at $T = \text{const}$. (Fig. 13c), where the number of points is also equal to the number of i experiments with various heating rates w_i. As can be seen from numerous



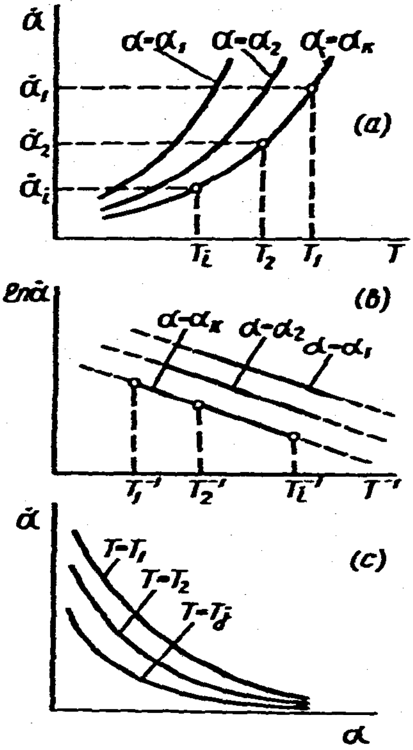


Fig. 12. Graphic illustration of obtaining the kinetic law.
(a) $\Delta T = \Delta T(w, t)$; (b) $T = T(w, t)$; (c) $\alpha = \alpha(w, t)$; (d) $\dot{\alpha} = \dot{\alpha}(w, t)$.

Fig. 13. Graphic illustration of obtaining the kinetic law.
(a), (b) $\dot{\alpha} = \dot{\alpha}(T)$ at α = const; (c) $\dot{\alpha} = \dot{\alpha}(\alpha)$ at T = const.

calculations, the first way of finding the function $\dot{\alpha} = \dot{\alpha}(T, \alpha)$ is somewhat more convenient, though the second one directly gives a form of function f(α).

Further processing of curves $\dot{\alpha}(T)$ at α = const. or $\dot{\alpha} = \dot{\alpha}(\alpha)$ at T = const. is carried out by the standard methods for chemical kinetics, i.e., a form of equation describing these curves is chosen, its entering parameters are found and a functional dependence $\dot{\alpha} = \dot{\alpha}(T, \alpha)$ is represented in the analytical form. In this case, the kinetic equation obtained either reflects the known reaction types, or is purely empirical.

The suggested scheme of non-apriori recalculation of non-isothermal data for isothermal conditions is considerably simplified for TG experiments. Having the data on dependences $T = T(w, t)$ from the experiments (it should be stressed that a temperature has to be measured in the operating cell), $\alpha = \alpha(w, t)$ at various heating rates w_i (Fig. 12c) and the corresponding curves $\dot{\alpha} = \dot{\alpha}(w, t)$ (Fig. 12d) obtained by graphical differentiation with respect to time of the curves $\alpha = \alpha(w, t)$, we shall obtain the dependences $\dot{\alpha} = \dot{\alpha}(T, \alpha)$ following the above-mentioned procedure (Fig. 13a) and so on.

The procedure of treating the experimental results obtained with a scanning calorimeter (DSC) slightly differs from the schemes of appropriate DTA and TG.

From the curves of changes in heat release rate $\dot{q} = \dot{q}(w, t)$, the general quantity of heat released by a given moment of time $q = q(w, t)$, and temperature in the operating cell $T = T(w, t)$ making use of the experimentally determined value of thermal effect Q the dependences $\alpha = \alpha(w, t)$ and $\dot{\alpha} = \dot{\alpha}(w, t)$ are found to be

$$\alpha = \frac{q(w, t)}{Q}, \dot{\alpha} = \frac{\dot{q}(w, t)}{Q}$$

Further processing is similar to that mentioned above. The method described is extensively used when studying the kinetics of thermal decomposition of various systems[30-32] by DTA and TG methods. Boundaries of applicability of this method will be discussed below.

IV. EXPERIMENTAL METHODS USED FOR STRAIGHTENING OF TEMPERATURE AND DECREASE OF SELF-HEATING

Let us consider now methodical techniques aimed at the correct experimental procedure of studying the chemical reaction kinetics under the regimes of programmed heating.

It has already been noted above that commercially produced devices for thermal analysis are not designed specifically for kinetic studies. Therefore, an arrangement of the operating cell does not often permit to determine clearly the conditions of its heat exchange with surroundings. This impedes a quantitative processing of experimental data and makes questionable the accuracy of the kinetic parameters to be determined.

Special means which provide such experimental apparatuses and methodology that a scheme of processing, correct from a thermophysical viewpoint can be used for obtaining the kinetic data, have been proposed[5, 7, 30, 31].

A forced mixing of the reacting liquid is used[5] in order that the process can be described by an averaged equation system. This method is naturally not appropriate in the case of solid systems.

For the same purpose it has been suggested[7] to use a reaction cell with weak heat emission to the surroundings. This method provides a good temperature uniformity throughout the reaction volume both for liquid and solid systems. However, it does not exclude thermal explosion for highly exothermic reactions and hence does not extend a very narrow range of rates which can be used for studying the reactions of such a type.

The method of removing a space non-isothermality by simple decrease in the weighted amount down to several miligrams cannot be recognized as quite universal. For instance, by using this method it is impossible to study the kinetics of heterogeneous systems containing components with sizes in the order of millimeter fractions.

In addition to low heat exchange coefficients, it has been suggested[30, 31] to intensify the effect of temperature straightening and simultaneously to decrease the appearing heatings-up at the cost of high dilution of the reactant by an inert diluent with high heat conductivity. Such a method has a number of advantages. Firstly, a possibility of thermal explosion is completely eliminated for exothermic reactions (a transition to completely degenerated regimes at the cost of increase in parameter γ), which permits the processes with a great thermal effect to be studied at higher than usual temperatures, and the heating rates accepted in the thermal analysis to be used. Secondly, a spatial gradient is practically excluded, which permits correct calculations. In the third place, it is unnecessary to know thermophysical properties of the substance under study since the heating conditions are defined by properties of a diluent. Strictly speaking, it is impossible to take quantitatively into account the thermophysical properties of the substance studied in a non-isothermal kinetic experiment, since in the course of the experiment the composition of the reacting medium changes by the law which form is unknown as a rule even in the cases when a formal kinetic description of the process is determined. This circumstance is an additional argument in favour of the methods[30, 31]. Finally, it is now unnecessary to chose a standard substance for the differential scheme, since naturally, a diluent is taken as a standard. Two methods of dilution are suggested and used, viz., a mechanical method when a reactant is mixed with a powdered heat-conducting inert diluent and placed into the ampoule, and a thermal method, when a reactant in the form of a thin (< 1 mm) layer is placed between heat-conducting blocks (Fig. 14). The first method is applicable for studying homogeneous solid and liquid substances, while the second is used for heterogeneous condensed mixtures. In both cases a diluent substance of the same form and size as a reactant is used as a standard. The typical degree of dilution is 1 : 100. The diluent substance should not affect catalytically the reaction under investigation. As is seen from some experience of work, the choice of the diluent presents no difficulties.

Naturally, investigation of the reacting media ballasted so deeply is accompanied by appropriate decrease in a value of the output signal. However, use of standard

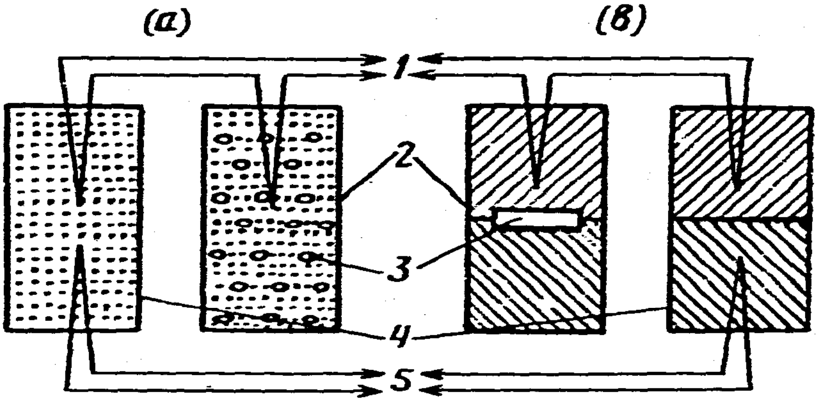


Fig. 14. Scheme of diluting a reactant by inert substance in thermography. (a) mechanical dilution; (b) thermal dilution.
1 = differential thermocouples; 2 = reaction cells; 3 = reactant; 4 = standard cells; 5 = thermocouples.

photogalvanometric amplifiers in measurement schemes of DTA-devices and scanning calorimeters permits a rather reliable recording of the processes under the same conditions. In thermogravimetrical installations using beam scales with preliminary balancing, employment of dilution within the limits mentioned does not lead to a decrease in accuracy when recording TG curves.

For mechanical dilution, aluminum cases were used with powdered aluminum oxide or powdered aluminum as an inert substance. For thermal dilution, thin-walled steel cases with inserted aluminum cylinders were used. In the lower cylinder there is a blind hole to accommodate a thermojunction, in the upper cylinder narrow holes (0.5 mm) are made to lead away gaseous reaction products. In the upper part of the case there is a bayonet lock which compresses the substance layer between butt ends of cylinders.

Let us illustrate the efficiency of the dilution method. Figure 15 depicts temperature distributions in the reaction cell calculated by numerical count of the system (6) at different time moments (to be precise, at various values of T_0) for concrete conditions of the thermographical experiment carried out on pyroxyline[30]. Kinetic parameters are taken for the monomolecular constant of reaction rate. It can be seen from Fig. 15 that at $w = 1\,°C\ min^{-1}$ a regime of thermal explosion is realized, while at

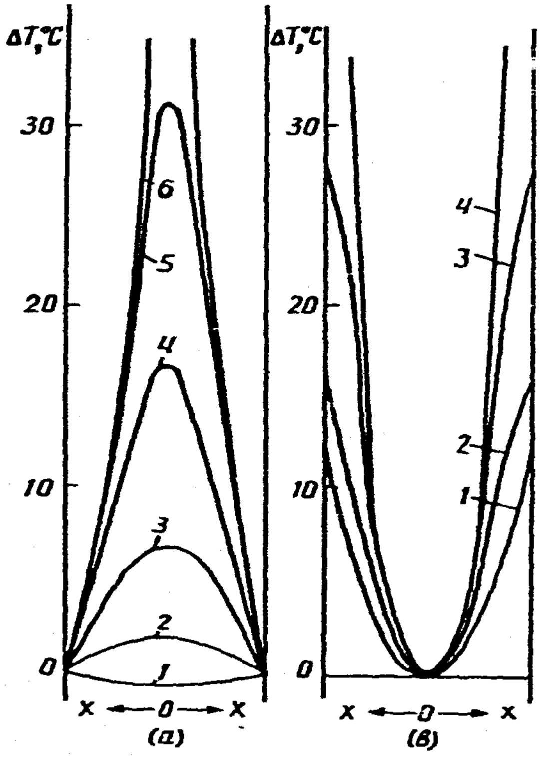


Fig. 15. Temperature distribution in the reaction cell of cylindrical form $r = 0.3$ cm (pyroxyline). (a) $w = 1\,°C\ min^{-1}$, counting of ΔT from the surface, T_0: 1 = 97°C; 2 = 164°C; 3 = 166°C; 4 = 166.6°C; 5 = 166.7°C; 6 = 166.71°C. (b) $w = 20\,°C\ min^{-1}$, counting of ΔT from the centre, T_0: 1 = 150°C; 2 = 207°C; 3 = 208.3°C; 4 = 208.4°C.

TABLE 1

CHARACTERISTICS OF THE TEMPERATURE FIELD IN THE CYLINDRICAL REACTION CELL = 0.3 CM FOR THE CASE OF PYROXYLINE DILUTION WITH ALUMINIUM OXIDE IN THE RATIO 1:100.
$\rho = 3.95$ g cm^{-3}, $\lambda = 6.10^{-2}$ cal cm^{-2}sec^{-1}deg^{-1}, $c = 0.18$ cal g^{-1}deg^{-1}.

Heating rate, w (*°C min^{-1}*)	*Quasi-stationary drop* $\Delta Tq = -\frac{wr^2}{4a}$ (*°C*)	*Maximum of difference,* ΔTm (*°C*)	*Ratio* $\frac{\Delta Tm}{\Delta Tq}$
1	−0.0045	−0.002	0.45
5	−0.0022	−0.0012	0.55
10	−0.045	−0.028	0.62
20	−0.09	−0.066	0.74

$w = 20$°C min^{-1} there takes place a regime of ignition, which completely excludes the possibility of obtaining quantitative kinetic data. Table 1 contains the calculation results for the case when pyroxyline is diluted with aluminium oxide Al_2O_3 in the ratio 1:100. In this case, the same activation energy and pre-exponential factor were taken for calculation as for Fig. 15, and the thermal effect is decreased by a factor of 100; thermal conductivity, thermal capacity and density are taken for Al_2O_3. It can be seen from the table that when using dilution over the whole range of rates 1–20°C min^{-1}, the regime of complete degeneration is realized. Here the maximum of temperature difference between the centre and surface is less than the quasi-stationary drop to the absolute value. Besides, it can be seen from the table that temperature drops can be neglected even at $w = 20$°C min^{-1}.

The experimental methodology and procedure of calculating the data obtained which is described above and in the previous chapter has been used[30–32] for investigating the thermal decomposition kinetics of a number of substances, viz., pyroxyline (DTA), polystyrene (TG), ammonium perchlorate (DTA and TG),

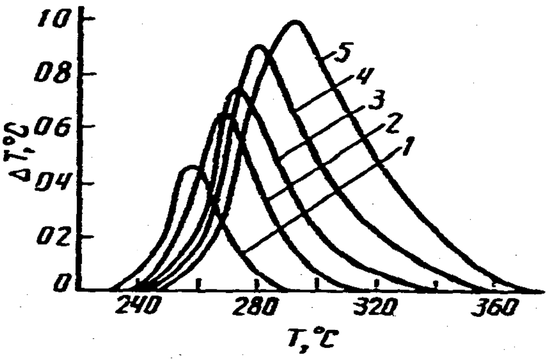


Fig. 16. Typical thermograms of decomposition of ammoniated copper chromate at various heating rates w (°C min^{-1}).
(1) 1.5; (2) 2.4; (3) 3.4; (4) 4.5; (5) 6.6.

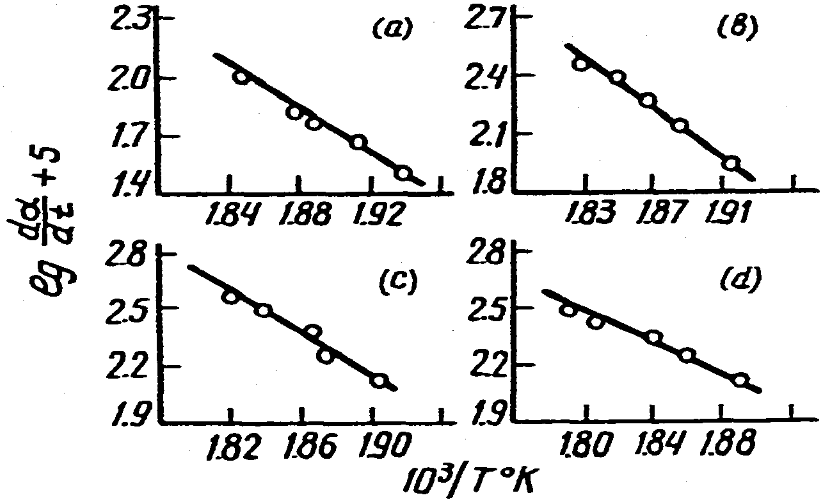


Fig. 17. Dependence of the decomposition rate of ammoniated copper chromate on temperature at fixed transformation degree α.
a = 0.1; b = 0.3; c = 0.4; d = 0.6.

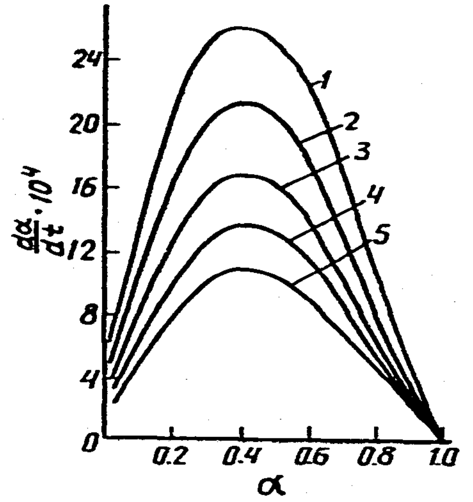


Fig. 18. Dependence of isothermal rate of decomposition of ammoniated copper chromate (sec^{-1}) on the transformation degree α at various temperatures (°C).
(1) 270; (2) 265; (3) 260; (4) 255; (5) 250.

mixtures of ammonium perchlorate and polymers (DTA and TG), ammoniated copper chromate (DTA). As an example, we shall give some data obtained when studying the decomposition kinetics of ammoniated copper chromate in vacuum[32].

Figure 16 shows the characteristic experimental curves of cell heating-up at various heating rates. Straightening in semi-logarithmic co-ordinates of curves $\dot{\alpha}(T)$ calculated from eqns (28)–(30) permits the temperature dependence of reaction rate to be determined at a fixed value of transformation degree α (Fig. 17). Figure 18 shows a dependence of isothermal decomposition rate on transformation degree $\dot{\alpha} = \dot{\alpha}(\alpha)$ at $T = \text{const}$. The data obtained are well described by the first-order equation of autocatalysis

$$\dot{\alpha} = k_1(1 - \alpha) + k_2\alpha(1 - \alpha)$$

Expressions for rate constants k_1 and k_2 (sec^{-1}) on Arrhenius treatment of experimental results (Fig. 18) are of the form

$$k_1 = 5 \cdot 10^7 \exp\left(-\frac{28000}{RT}\right)$$

$$k_2 = 6.3 \cdot 10^8 \exp\left(-\frac{26500}{RT}\right)$$

V. ON THE LIMITS OF APPLICABILITY OF THE NON-A PRIORI METHOD FOR RECALCULATING THE DATA OF A NON-ISOTHERMAL EXPERIMENT TO ISOTHERMAL CONDITIONS

Let us now consider some factors which limit the possibility of applying the non-apriori method discussed in chapters III and IV. First of all, this refers to stage and diffusion difficulties. The calculation procedure discussed is applicable only for single-stage reactions when the process is described by one kinetic equation. There are quite a number of such reactions. These are simple reactions of the order n, reversible reactions, reactions with auto-catalysis and others. It is of interest that in some cases (for instance, in the case of autocatalysis), two kinetic constants with different activation energies enter the equation. In this case, a kinetic function cannot be represented in the form of (24) and many calculation schemes which make use of such an expression become unapplicable. The method given permits not only to notice availability of several constants with different activation energies[*], but also to determine their values at different temperatures (see an example at the end of Chapter IV). This method cannot be applied for studying complex reactions with consecutive and parallel stages. This question has been discussed in detail[2]. The main characteristic property of complex reactions consists in the fact that a state of the system is not characterized by two magnitudes T and α, as is accepted in the scheme considered and takes place for single-stage reactions, but depends also on the way in which the system came up to this state, i.e., on the pre-history of the process. As shown[2], the equation which describes a two-stage reaction is of the form

$$\frac{\ddot{\alpha}}{F(T, \alpha, \dot{\alpha})} - \frac{\dot{T}}{\psi(T, \alpha, \dot{\alpha})} = 1 \qquad (31)$$

i.e., it is determined by two functions of three variables. To find these functions from the non-isothermal experiment is a complicated and unsolved problem. However, a

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[*] This appears as dependence of the efficient activation energy on transformation degree.

criterion can be pointed out when a single-stage approach is valid. It is evident that for this purpose the heating-up should be realized in such a way that one and the same state T, α can be approached with different "pre-history". As follows from paper[2], to do this it is necessary to realize heating-up with two parameters A and B. On processing the experimental data on the single-stage scheme at A = const. and B = var., one can obtain

$$\dot{\alpha} = \dot{\alpha}_A(T, \alpha)$$

If it turns out that a form of $\dot{\alpha}_A$ does not depend on value A, then the process is single-stage and the expression obtained is sufficient for its description. If $\dot{\alpha}_A$ are different for various A, then the method under consideration is unapplicable.

How can a two-parametric heating-up be realized? A linear heating cannot be applied for these purposes, since it is characterized by one parameter w. A static heating is not adequate either for the same reason (one parameter T_0). For these purposes it is convenient to realize the heating by the parabolic law

$$T = T_i + w_i t + \frac{at^2}{2}$$

where w_i is an initial heating rate, a is heating acceleration. Here w_i may play a role of parameter A, and a of parameter B. You may act in a different way, viz., two series of the experiment may be performed: one under the static conditions (T_0 = const.), and the other under linear heating (w = const). For a single-stage reaction, a form of $\dot{\alpha}(T, \alpha)$ obtained by these two ways, should be identical.

Another approach to evaluation of applicability of a single-stage scheme is possible, based on purely kinetic considerations. As is known, kinetics of chemical reactions can be studied by different methods, viz., from heat evolution, from changes in weight, from increase in pressure, from changes in volume of gaseous products. For single-stage processes, changes of these values are usually proportional to transformation degree, i.e., for single-stage processes one may write

$$\frac{q}{q_\infty} = \frac{\Delta m}{\Delta m_\infty} = \frac{\Delta p}{\Delta p_\infty} = \frac{\Delta V}{\Delta V_\infty} = \alpha \tag{32}$$

where q is quantity of heat evolved by the given moment of time, m mass, p pressure, V volume, sign ∞ denotes the end of transformation.

If under the identical heating conditions the values obtained by different methods in accordance with (32) are the same, i.e., curves $\alpha(t)$ coincide, one may expect the absence of staged effects and use the single-stage scheme.

In some cases a strong distribution of reactant concentration connected with diffusional (filtration) processes may be an important limitation for application of the approach discussed. For instance, such a situation may arise in reactions occurring with participation of the gaseous phase. On oxidation of metal powders in air, diffusion may limit the access of oxygen to internal layers of a weighted amount and lead to irregular reacting. As is known, on decomposition of some substances, an autocatalysis by gaseous products is observed. Diffusion processes of product removal from the reaction zone may have a profound effect on the reaction rate in these cases. Other examples of the distorting role of diffusion may be given. The approach discussed can certainly not be applied in the complicated diffusion situation, since it does not consider the processes of substance transfer. However, in many cases substance transfer does not take place, or it is negligible. For instance, this occurs in air-tight cells at thermal decomposition with formation of inert gaseous products, at polymerization processes, at oxidation in the kinetic region and so on. In some systems the substance transfer is realized only inside the reactant without exchange with the surroundings. In this case the diffusion processes are treated as kinetic and affect the form of the kinetic equation, rather than the scheme for processing the experimental curves. Among these processes are reactions of synthesis from elements in the solid phase. Diffusion processes of interaction between grains of elements (for instance, of titanium and soot) define here a form of the kinetic law. The rate of diffusion processes of interaction between a reactant and an ambient gas greatly depends on a mass of weighted amount and its geometrical sizes. Therefore, the following simple criterion of validity of the method suggested can be proposed—a form of the kinetic function $\dot{\alpha}(T, \alpha)$ must not depend on the mass of weighted amount (or on the length of diffusion path), i.e., the form of $\dot{\alpha}$ should be the same at p = const. in open cells, and at $m/V =$ const. in air-tight cells.

Stage and diffusion difficulties are the most important factors which limit the possibility of applying the given variant of the non-isothermal method.

VI. CONCLUSION

As is seen from the foregoing, the main problems which are now solved in the theory of non-isothermal methods are creation of concrete conditions for performing the experiment and discovering the most general scheme for processing thermograms. Solution of these problems is now nearing completion. It is already clear that the main point in the organization of the experiments realized at linear heating is to provide temperature uniformity in the reaction cell. To do this, it is necessary to know the conditions for heat exchange and to be able to control them in the proper way. The value of self-heating is of no fundamental significance, since it is taken into account when processing experimental data. Therefore, the desire of experimentators to decrease self-heating and hence to increase an accuracy of temperature measurement is unjustified. It is of interest that the availability of self-heating significantly distorts a linear course of temperature in the reaction cell. Therefore one should not aspire to strictly keep a linearity of changes in temperature in the heating device (standard). Of course, absence of self-heating and keeping of heating linearity simplify to some extent the procedure of kinetic calculations. However, advantages are insignificant and do not compensate methodical difficulties and limitations.

A question is often discussed in the scientific literature whether it is necessary to know a value of the coefficient of heat exchange between a reaction cell and a heating device. It follows from the foregoing that knowledge of value *h* is necessary, firstly, for providing uniform temperature distribution in the reactant; secondly, for determining the rate of heat release in the DTA method (value *h* enters the equation of thermal balance). There are situations when knowledge of *h* is not necessary (for instance, a thermogravimetrical experiment with temperature measurements in the reaction cell and the controlled provision of low temperature gradient there). However, they should be considered as an exception to the rule.

Thus, creation of gradientless temperature field in the reaction cell, measurement of time dependence of its temperature, knowledge of the heat exchange coefficient between the reactant and the heating device—all these are the main features of the modern experiment which makes it possible to study correctly the kinetics of chemical reactions under the conditions of programmed heating.

Unfortunately, experience in theoretical investigations and practical recommendations have not yet been used properly when designing thermographs (derivatographs, scanning calorimeters). The main attention here is so far paid to the problems of the electronic-measuring technique, while thermo-technical problems are ignored. Creation of cells with organized heat exchange is a primary problem in this field.

However, it should be expected that in the nearest future correct conditions will be provided for the kinetic experiment at programmed heating.

A question of principle now arises. How can one obtain in full the extensive kinetic information which the non-isothermal experiment contains? This problem should result in setting theoretical studies of a new type where the main stress will be on a generalized description of staged processes. The non-isothermal method has the greatest advantages as compared to the isothermal method just as applied to complex reactions. However, it is already clear now that this problem is very complex and for its solution not only a deep analysis of kinetic regularities is required, but a significant development of the experimental technique.

Application of the generalized approach to investigation of complex reactions, which reduces to search many functions of many variables*, is possible only when making use of modern EC with large memory and rapid action. Now only the simplest kinetic problem is solved (the description of single-stage reactions) and the results can easily be presented in the form of kinetic equations. The form of presentation of the result when studying complex reactions should be significantly different. Kinetic functions will be stored in EC memory and used when calculating various non-isothermal processes. The heating regimes should be changed. Linear heating, as has been already noted, limits the possibilities of studying stage reactions, and therefore more complicated forms of heating are preferred here depending on several parameters. Parabolic and harmonic laws of heating seem to find application in the future.

Thus complex heating, usage of many kinetic functions for experiment descrip-

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* As we can see, two-stage processes are described by two functions of three variables.

tion, wide application of electronic computers are all characteristic features of a new stage in the development of theory and practice of non-isothermal kinetics.

The interest in non-isothermal methods of investigation is very wide and continues to develop. This is connected with the fact that there exists a constant contradiction between extensive information of the non-isothermal method and difficulties of its "extraction".

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