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AUTOMATED SYSTEM FOR KINETIC RESEARCH IN THERMAL ANALYSIS

II. Organization of kinetic experiments in ASKR

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The correctness of a kinetic experiment is an essential condition for obtaining reliable results in kinetic investigations. Methods for provision and testing of thermo-physical and concentration correctness are discussed in the present article. Problems connected with the non-isothermal mode of an actual thermoanalytical experiment caused both by programming and by heat release in the sample are considered. Application analysis of the combined partial-linear heating laws in kinetic investigations is given in relation to the heat flux calorimeters 'SETARAM'.

Keywords: automated system for kinetic research

Introduction

Realization of kinetic investigations by means of an automated system for kinetic research (ASKR), described in [1], can yield reliable results only in the case of correct experiment organization.

In thermal analysis (including calorimetry) the principles of kinetic experiment organization must be considered on the basis of apparatus scheme analysis.

The main element of the apparatus is the measuring block having definite constructive peculiarities. The measuring block consists of the reaction cell (reactor), sensor (or system of sensors) and heating block. Accordingly, the experimental characteristics are determined by three factors:

- mode of reactor operation;
- temperature range of the heating block;
- construction and type of sensor.

According to this scheme we will consider the main methodological problems connected with carrying out of a correct kinetic experiment.

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Correctness of a kinetic experiment

Any investigation must be carried out under conditions of reactor operation which allow the simplest interpretation of the data obtained. In respect of kinetic studies it is necessary to exclude as far as possible the influence of heat and mass exchange on the process, i.e. to provide uniform distribution of temperature and reagent concentrations in the sample (thermophysical and concentration correctness, respectively). This demand is made because almost all known methods of kinetic analysis are based on the model of such non-gradient reactors, named further as kinetic reactor.

The role of heat- and mass exchange depends markedly on the reactor type and the characteristics of reacting sample under investigation. Two reactor types are used in thermal analysis as a rule:

- closed batch reactor;
- open batch reactor (it should be noted that in this case the reactor includes not only the reaction cell but also the sample holder, the elements of pneumatic system and so on).

Reactors of the first type are widely used in DSC and DTA instruments for studying chemical processes in solid and liquid state (thermal decomposition, polymerization, reactions in multi-reagent mixtures and so on). The investigator may use an atmosphere of desired initial composition inside the reactor which is changed only by the gaseous products evolving in the chemical reaction. For these reactors thermophysical correctness is the main problem which is discussed indetail in [2].When the experiment is correct from the thermophysical point of view and the starting reaction mixture is uniform, concentration gradient formation has a small probability.

Reactors of the second type are typical in thermogravimetry. They are also used in DSC and DTA for studying thermal decomposition, dehydration, gas-solid reactions and so on. In many cases it is effective to apply continuous flow reactors (for one of the reagents), but such reactors can be used in hardly any commercial instrument except heat flow calorimeters DSC–111 and C–80 'SETERAM' and RC–1 'METTLER'.

Mass exchange factors play an important role in open and continuous flow reactors. The problem of concentration correctness is discussed in [3]. It is shown specifically that continuous flow reactors make it possible to carry out correct kinetic experiments in a significantly wider range of conditions compared to open batch reactors thanks to methods developed for mass exchange organization.

Various methods can be used for thermophysical correctness provision (both separately and in a combination):

- employment of small rates of temperature change (it may be recommended to use heating rates less than 2 K/min in kinetic experiments);

- carrying out the experiment with a minimum sample mass (but it should be taken into account that for multicomponent samples mass reduction may lead to an irreproducibility of the results because of composition fluctuations);
- distribution of the substance in thin layer on the bottom and at the walls of the reactor;
- heat dilution of the sample with inert substances having high heat conductivity [4];
- insertion of a flat or coaxial insert made of the inert high heat-conducting material into the reactor [5].

Sometimes the sample is encapsulated before inserting into the reactor (for example it is soldered in a glass ampoule). In such cases the air gap between the capsule and reactor walls must be filled with any high heat-conducting substance (liquid or powder-like).

It is necessary to mix carefully powder- or paste-like multicomponent samples before the experiment to avoid initial inhomogeneity.

The best way to exclude temperature and concentration gradients in liquids is mixing [6]. Natural convection helps to establish uniform distribution for liquids with low viscosity. The mixing method depends on the construction of the instrument. For example the calorimeter type C–80 allows to mix reagents by swaying the measuring block or by using a stirrer built into the reaction cell. Effective forced mixing is provided in the Mettler reaction calorimeter type RC–1. Natural convection is the only type of mixing in some other thermoanalytical instruments.

The non-uniform temperature distribution in a sample may be diminished essentially by means of reducing the heat exchange between the reactor and heating block [7]. But in this case the temperature of the sample has a complicated dependence on time, and interpretation of the data is difficult. Furthermore, the intensity of heat exchange in commercial instruments is determined by their construction and sensor type and cannot be varied.

For estimating the quality of experiment it is necessary to use any appropriate method of correctness analysis and quantitative criteria of correctness. It is evident that any direct examination of correctness (i.e. measurement of the real temperature and concentration gradients in the reactor) is practically impossible. Therefore, let us consider some indirect experimental and computing methods.

Experiment correctness examination means carrying out test experiments in the widest possible range of conditions (various heating program, degrees of heat dilution, flow rates of reagents in flow reactors, gas pressures and so on). The main signs of correctness are:

- no contradiction in the total combination of the results obtained
- possibility of combined data description in kinetic analysis.

In some cases it is reasonable not only to vary the experimental conditions but also to measure the changes of other properties of the reacting system for inspection of the kinetic regime (i.e. to consider the additional information about the process). Let us consider results concerning the thermal decomposition of sodium carbonate peroxyhydrate:

$$Na_2CO_3\cdot 1.5H_2O \rightarrow Na_2CO_3 + H_2O + O_2.$$

TG experiments carried out with various heating programs (linear and combined linear-isothermal) (Fig. 1) give non-contradictory data which are well described by an *N*-order reaction model. Evident signs of non-correctness are absent. However, DSC data obtained in similar conditions noticeably differ from TG data:

– in the linear heating mode the DTG curve is extended compared to the DSC curve (Fig. 1a);

– the rate of heat evolution decreases more rapidly than the rate of mass loss on the isothermal part of combined heating program (Fig. 1b).

The deviations observed are due to the fact that the rate of heat evolution is determined only by the decomposition of hydrogen peroxide inside the substance crystals during the entire the process, as the mass loss rate due to oxygen and water vapour evolution depends both on the decomposition rate and the diffusion rate of gaseous products through the constantly growing layer of sodium carbonate. Consequently the TG data are non-correct and the DSC data may be used for kinetic analysis since they present the dynamics of the chemical reaction itself.

The principle of computing methods is a mathematical simulation of the reactor operation by means of the kinetic model with consideration of heat- and mass-transfer. The model is obtained as a result of kinetic analysis of experimental data assumed to be correct. This procedure allows to estimate the deviations of temperature and concentration distributions from the uniform ones and to determine the difference between measured and calculated responses (DTA, DSC or TG data, reagent concentration and so on). The experiment may be considered as a correct one if calculated differences are less than the experimental errors of response measurements.

If ASKR these calculations are done by means of subsystem 'THERMAL EXPLOSION' which may be incorporated in the automated system [8].

In an experiment is considered as non-correct it must be repeated with the use of appropriate methods of correctness provision. All steps of data processing should also be repeated. So the kinetic investigation becomes an iterative procedure.

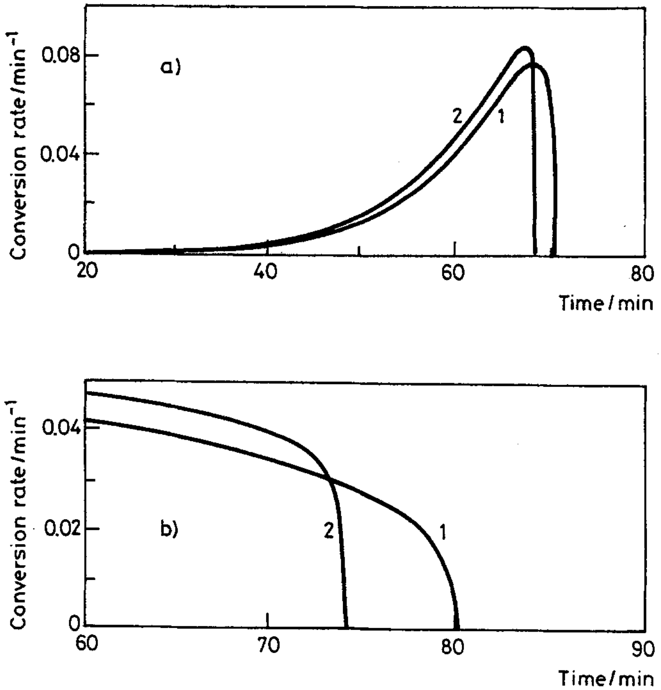

Fig. 1 Conversion rates during thermal decomposition of Na_2CO_3. a) linear heating program $T = 320 + B.t$, K; $B = 1$ deg/min; b) isothermal part of linear-isothermal heating program: $T = \begin{cases} 320 + B{\cdot}t, \text{K}, & B = 1 \text{ deg/min}, \ t, 60 \text{ min} \\ 380 \text{K}, & t > 60 \text{ min} \end{cases}$; 1 – TG-data; 2 – DSC-data

Temperature regimes of kinetic experiments

The typical peculiarity of kinetic experiments in thermal analysis is the non-isothermal conditions which arise either due to the application of programmed changes of heating block temperature or to the heat evolving in the sample which leads to a deviation of the sample temperature from the given heating program.

Let us consider some problems related to the non-isothermal modes of experiment for the heat flux calorimeters DSC–111 and C–80 'SETARAM'. The results obtained may be easily extended to instruments of other types taking into account their construction peculiarities.

Temperature programming

Linear heating or cooling is a traditional heating program in thermal analysis. The essential characteristic of linear heating is the establishment of the quasi-stationary regime in some time after the start of heating [9, 10]. In this regime the temperature gradient does not depend on time in any point of the block and the rates of temperature changes are equal in all points of the block.

The quasi-stationary regime is an obligatory condition for the correctness of kinetic. Furthermore, the peculiarities of the quasi-stationary field allow one to determine easily the relationships between the temperatures in various points of measuring block (simplified scheme of heat flux calorimeter block is presented in Fig. 2). Such a necessity appears specifically for the determination of sample and reference temperatures (T_s and T_r respectively) as these values are not measured directly as a rule. In practice it is convenient to use the relationship between T_r and known programmer temperature T_z. This relationship is determined by means of temperature calibration of the instrument [11, 12]. Deviations of T_s from T_r due to heat evolution and methods of their estimation will be discussed below).

Temperature calibration

Methods of temperature calibration depend on the instrument construction: the type of sensor and sample holder, the reaction cell size, the heat exchange organization between cell and other elements of the measuring block, the possibility to introduce temperature sensor into the cell and so on [11, 12]. (It should be noted that in thermogravimetry special methods of temperature calibration are used due to the peculiarities of the measuring system, but we do not consider this problem as it has been discussed in detail in [12].)

Calorimeter DSC-111 has a relatively small cell (diameter of DSC-cells is 6.5 mm, diameter of cells for TG experiments on TG-DSC–111 is 5 mm). Incorporation of any temperature sensor in such a cell causes an essential distortion of T_r due to the heat loss throughout the sensor wires even if appropriate steps are

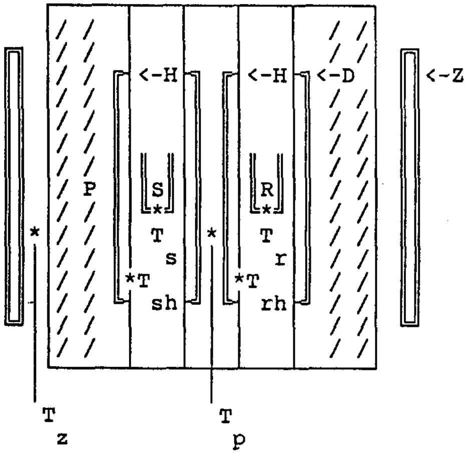

Fig. 2 Measuring block scheme of heat flux calorimeter. *D* – fluxmeter; *P* – heating block; *Z* – heater; *S* – sample; *R* – reference; *H* – sample/reference holder. T_z – programmer temperature; T_p– heating block temperature. T_s and T_r – sample/reference temperature; T_{sh}, T_{rh} – sample/reference holder temperature

made for its reduction. Hence the most adequate way for temperature calibration is based on phase transitions of materials having wellknown transition temperatures. For a chosen set of standards the experiments are carried out with several heating rates. The temperature correction $\delta T = T_z - T_r$ depends not only on the given heating rate B_z but also on the value T_z. This fact is due to the alteration of both the thermophysical properties of construction materials applied in the measuring block and the heat exchange conditions between the cell and the sample holder.

The dependence $\delta T(B_z, T_z)$ which allows to calculate the reference temperature T_r with the use of known value T_z may be determined by means of regression analysis methods [13]. For DSC–111 and TG-DSC–111 the value of DT is presented as

$$\delta T_z = T_r - T_o = a_1 + a_2 \cdot B_2 + a_2 \cdot T \qquad (1)$$

Such calibration dependence based on the data obtained for an accepted set of standards [12] In-Sn–Pb–Zn allows to determine T_r in the temperature interval 150°–420°C with an error less than 0.1°C. Furthermore, extrapolation of expression (1) to the ranges 20°–150°C and 420°–600°C gives satisfactory results (error of T_r is about 0.2°C). For diminishing the error in larger temperature interval it is necessary to use a larger set of standards.

Analysis of formula (1) leads to two essential conclusions. Firstly, the true heating rate B_r differs from the given value B_z:

$$B_r = B_z \cdot (1 - a_2) \qquad (2)$$

Secondly, the reference temperature differs from the programmer temperature even in the isothermal mode:

$$\delta T(B_z = 0) = a_o + a_2 \cdot T_z.$$

Let us consider some quantitative results of DSC–111 calibration. The value of correction is about 4°C for $T_z = 500°C$ and $B_z = 5$ deg/min. As for the true heating rate, its deviation from the given value is about 0.2% and the corresponding correction may be neglected (for $B_z = 5$ deg/min and experiment duration $t = 100$ min the calculated temperature interval is $T_{zo} + B_z \cdot t = 500°C$, and the true temperature interval is $T_{ro} + B_r \cdot t = 499°C$. Deviations between T_z and T_r in isothermal conditions are also small, for example δT is 1°C for $T_z = 500°C$.

The calibration of the C–80 instrument may be done in the same way, but in this case it is reasonable to use direct measurement of the reference temperature because the reaction cell of this instrument is comparatively big (its diameter is 17 mm and height 80 mm). T_r is measured for different heating rates and for a number of isothermal plates in the whole temperature interval. The results are processed as in the previous case. Such calibration method may be used for other heat flux calorimeters with big cells (for example, HT–1500, BT 2.15, MS–80).

The dependence $\delta T(B_z, T_r)$ has a more complicated character for C–80 compared to DSC–111:

$$\delta T = T_z - T_r = a_o + a_1 \cdot B_z + a_2 \cdot T_z + a_3 \cdot B_z \cdot T_z + a_4 \cdot T_z^2. \qquad (3)$$

The error of δT depends on the error of temperature measurement and is usually 0.1–0.2°. The true heating rate may be calculated according to the formula:

$$B_r = B_z \cdot (1 - a_2) - a_3 \cdot B_z^2 - 2 \cdot a_4 \cdot T_z \cdot B_z. \qquad (4)$$

Consequently, for C–80 the true heating rate also depends on temperature, but this dependence is very weak (at least for rates less than 0.5 deg/min) because of the small value of a_4.

The values of dT for C–80 are relatively big, and even in isothermal mode they may reach several degrees (Fig. 3), therefore a precise temperature calibration is of great importance.

Combined partially linear heating program

The information provided by a kinetic experiment may be increased by using more complicated nonlinear heating programs. For example, the method considered in [14] enables one to synthesize optimal temperature programs for investigating multistage chemical reactions. According to [14] it is possible to use the combined partially linear combined heating program instead of a non-linear one. Such mode combines regions of linear heating with different rates. Any of these regions may be isothermal as well. At present these combined programs are widely used and now they are realized in instruments produced by of such firms as 'SETARAM', 'NETZSCH' and some others.

Using these combined heating programs it is possible to investigate the kind of kinetic function in more detail. In particular, application of the linear-isothermal heating mode allows to get the process on the required level of reaction rate in controlled temperature conditions and then to continue the experiment in the isothermal mode. Let us consider the experimental results for the thermal decomposition of 1,2-dinitroethylene glycol (Fig. 4). Data obtained in the linear-isothermal experiment distinctly reveal the autocatalytic character of the process.

One of the main problems connected with the application of combined heating programs is the presence of transition regimes. The transition from one quasi-stationary regime to another causes a change in the temperature gradient in the heating block. The temperature of the sample changes in a rather complex manner (Fig. 5). If the experiment is carried out with constant heating rate, the establishment of the quasi-stationary regime (initial part) occurs in the temperature interval where the chemical reaction is still absent. In this case T_r can be calculated using linear heating program with the correct values of starting temperature T_{ro}

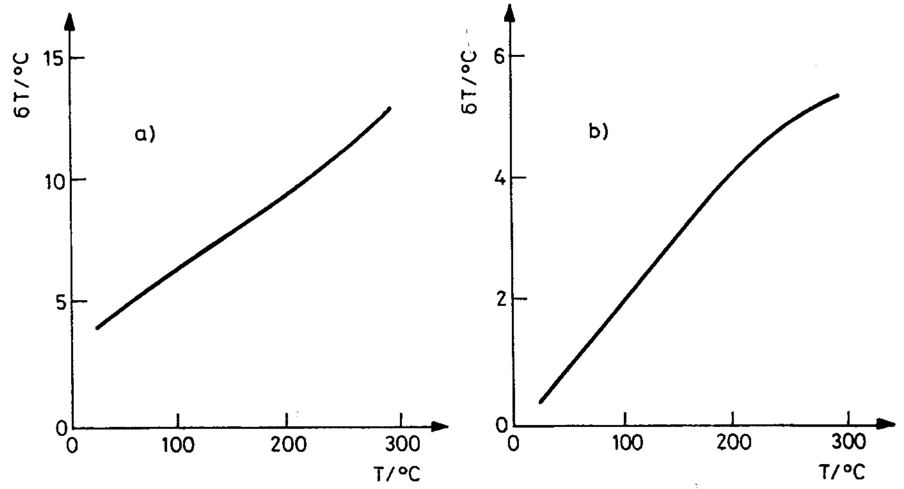

Fig. 3 Temperature dependence of $\delta T = T_z - T_r$ for calorimeter C–80. a) linear heating mode, $B_z = 0.5$ deg/min; b) isothermal mode

and heating rate B_r. The correction of T_{ro} is made by extrapolation of the linear part of the temperature plot up to the starting time (Fig. 5):

$$T_r = T_{ro} + B_{r1} \cdot t\,; \quad t < t_1\,; \quad T_{ro} = T_{zo} - \delta T_1 \tag{5}$$

In the case of a combined program the transition from one regime to another is realized when the conversion in the sample already occurs. Data processing for such experiments must be done using rather complicated relationships for the true temperature change $T_r(t)$ like

$$T_r = \begin{cases} T_{ro} + B_{r1} \cdot t, \; t < t_1 \\ T_{r1} + B_{r2} \cdot (t - t_1) + (\delta T_1 - \delta T_2) \cdot (1 - e^{-(t - t_1)/\tau}) \end{cases} \tag{6}$$

where B_{ri} and δT_i are heating rate and temperature correction in the i-th region.

This expression has been obtained for a heating program consisting of two regions with different rates, but one of the heating rates may be equal to zero. The same expression may also be used for heating programs with more than two parts. The time constant τ characterizes the heat inertia of the block and must be determined for every type of instrument. For example, the time constants for the TG-DSC–111 and C-80 instrument is 1 min and 10 min, respectively.

For such complicated dependence of $T_r(t)$ it is more difficult to perform a kinetic analysis of experimental data. The question arises if it is possible to use approximate partially linear dependence $T_r^a(t)$ instead of a true one in the kinetic analysis. Such an approximation (Fig. 5) is:

$$T_r^a = \begin{cases} T_{ro} + B_{r1} \cdot t, & t < t_{r1} \\ T_{r1} + B_{r1} \cdot t_{r1} + B_{r2} \cdot (t - t_{r1}) \end{cases} \tag{7}$$

where t_{r1} is the corrected value of time corresponding to the end of the first part:

$$t_{r1} = t_1 + (\delta T_1 - \delta T_2)/(B_{r1} - B_{r2}). \tag{8}$$

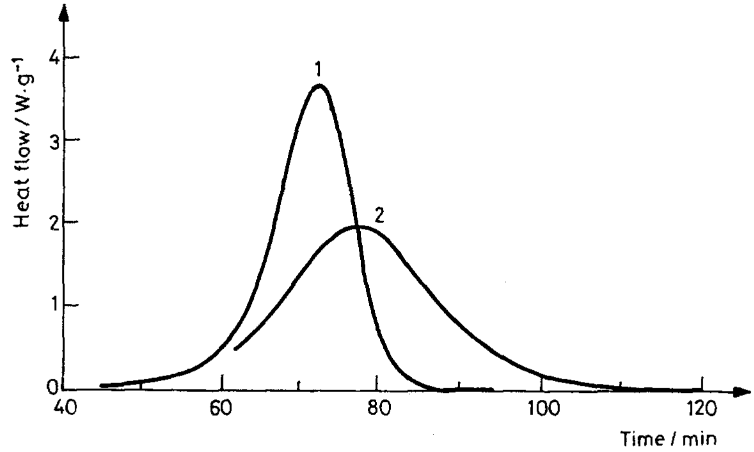

Fig. 4 Rates of heat evolution during thermal decomposition of 1,2-dinitroethylene glycol 1 – linear heating mode: $T = 390 + B \cdot t$, K, B=1 deg/min; 2 – isothermal part of linear-isothermal heating program: $T = \begin{cases} 390 + B \cdot t, \text{ K}, & B = 1 \text{ deg/min}, \ t < 60 \text{ min} \\ 450 \text{ K}, & t > 60 \text{ min} \end{cases}$

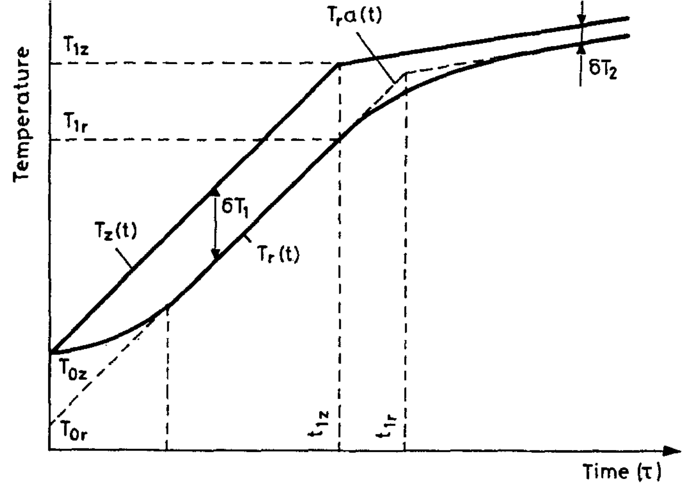

Fig. 5 Substance temperature change under conditions of combined heating program. j – part number; δT_j, B_j – temperature correction and heating rate on the j-th part; T_{j-1}, T_j – start and final temperatures on the j-th part; t_{j-1} and t_j – times corresponding to beginning and end of the j-th part; $T(t)$ and $T^a(t)$ – true and approximate heating

For calorimeters DSC–111 and C–80 the value of t_{r1} determined by the following expression (Eqs (1) and (2)):

$$t_{r1} = t_1 + a_2. \tag{9}$$

The usefulness of the described approximation may be established by means of calculating the kinetic curves for the true and approximate programs of the temperature change in the substance and a comparison of these curves (the possible overheating due to chemical reaction has been neglected). The results of simulation for the DSC-111 instrument in the linear-isothermal mode are shown in Fig. 6:

$$T_{ro}= 100°;\quad B_{r1}=5 \text{ deg/min};\quad B_{r2}=0 \text{ deg/min};\quad t_2=20 \text{ min};\quad \tau=60 \text{ s}.$$

The results of the computing experiment allow us to make some important conclusions:

1. The difference between the curves obtained for true and approximate heating programs is significant only in the transition regime with duration t_{tr} about (4–5) τ.
2. After the quasi-stationary regime has established the difference between the curves obtained for the true and approximate heating programs is less than the experimental error.

Computing experiments show that these conclusions are true for processes with different activation energies and various types of kinetic functions. The conversion in the transition point between different modes does not play any considerable role either.

It should be stressed that only non-distorted parts of kinetic curves can be correctly used in kinetic analysis, consequently the total chemical reaction time in experiments with partially linear heating modes should be considerably greater than the total time of transition regimes.

The duration of the transition regime t_{tr} can be simply determined from the transition of one heating mode to another. For example, the transition time t_{tr} for DSC–111 is equal to 3–4 min and for C–80 it is about 35–45 min.

The partially linear heating program can be used to investigate isothermal process with high rates, when (Fig. 7) the traditional isothermal experiment is incorrect.

Application of the linear-isothermal heating program makes it possible to raise the reacting substance into required temperature level in controlled conditions and to obtain non-distorted data suitable for kinetic analysis.

Temperature of the reacting substance

Enthalpy changes resulting from chemical reactions may cause overheating of the sample compared to the reference. The relationship between the values T_s and T_r in this case may be given as:

$$T_s = T_r + \delta T, \tag{10}$$

where δT is the value of overheating.

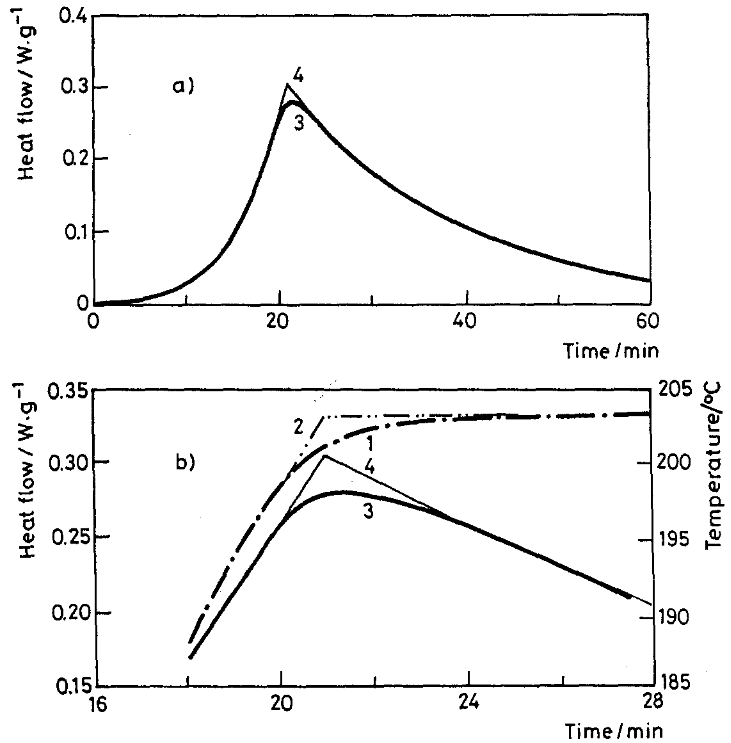

Fig. 6 Curves of heat evolution rates for linear-isothermal mode. a) – full kinetic curves; b) – fragments of kinetic curves corresponding to the transition regime 1 – true temperature change function $T = T_r(t)$; 2 – approximate temperature change function $T = T_r^a(t)$; 3 – kinetic curve corresponding to the true heating function 4 – kinetic curve corresponding to the approximate heating function

The sign of δT is determined by the sign of the reaction heat effect and the magnitude of δT depends on the heat capacity of the sample and the ratio of the heat release and heat removal rates.

A complicated character of the function $T_s(t)$ makes kinetic analysis of experimental data much more difficult.

A simple approximate criterion is proposed in [2]:

$$\delta T_{\max} < \varepsilon \cdot \frac{RT_{r}^{2}}{E} \qquad (11)$$

where $dT_{\max}$ is maximal overheating, ε – experimental error of rate determination, T_r – reference temperature in the point of maximal overheating, R – universal gas constant, E – activation energy of the chemical reaction.

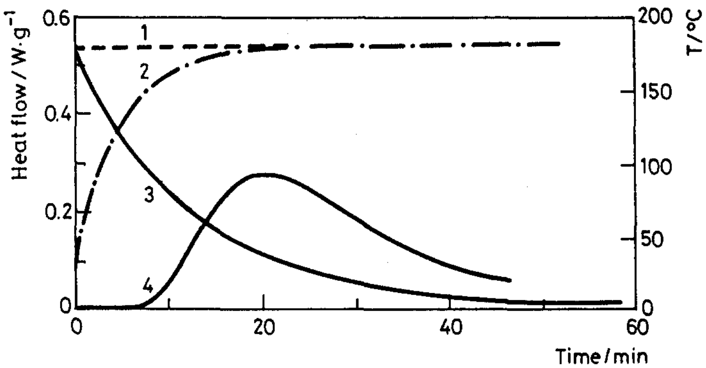

Fig. 7 Distortion of the kinetic curves in static experiment because of the substance temperature change 1 – temperature of the heating block; 2 – substance temperature; 3 – ideal isothermal kinetic curve; 4 – real kinetic curve

Inequality (11) is valid for a simple N-order reaction model. However, this criterion can also be used for more complicated processes. In this case the value E must correspond to the stage with the largest heat effect.

Finally, it should be noted that the method of kinetic analysis applied in the automated system of kinetic research (ASKR) does not put any limitations on the mode of temperature changes.

Conclusion

Although the basic problems connected with kinetic experiments the correctness and general methods of their evaluation are common for kinetic research in general, nevertheless, it is practically impossible to give universal recommendations on correct kinetic experiment organization for all cases. The reason is that various thermoanalytical instruments used in kinetic investigations are characterized by a great variety of constructions. The processes under investigation may also be widely different. Hence it is necessary to analyse the problem of correctness for each type of instrument and for every process. In this article we considered the solution of this important problem mainly in reference to heat flux calorimeters but the methodology developed can be applied for other types of instrument.

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Zusammenfassung — Die Korrektheit eines kinetischen Versuches ist eine wesentliche Voraussetzung, um in kinetischen Untersuchungen zuverlässige Ergebnisse zu erhalten. In diesem Artikel werden Methoden zur Bestimmung und zum Testen der Richtigkeit hinsichtlich der Thermophysikund und der Konzentrationen beschrieben. Dabei werden Überlegungen zu Problemen bei nichtisothermen thermoanalytischen Versuchen angestellt, die sowohl durch Programmierung als auch durch Wärmefreisetzung verursacht werden. In Bezug auf das Wärmeflußkalorimeter "SETARAM" wird eine Analyse der Anwendung des Gesetzes der kombinierten partial-linearen Erhitzung in kinetischen Untersuchungen beschrieben.