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AUTOMATED SYSTEM FOR KINETIC RESEARCH IN THERMAL ANALYSIS

I. General description of an automated system

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Kinetic research with employment of thermal analysis methods comprises a complicated multi-stage procedure. The full performance is impossible to be achieved without automation of all the stages with regard to their interconnections. Development of the automated system for kinetic research (ASKR) in thermal analysis is the solution to this problem.

ASKR is described as based on the complex of thermoanalytical devices of the 'SETARAM' company. The system allows reducing the time of measurements and ensures high quality and reliable results.

The structure, purpose and potentialities of ASKR are considered, methodological questions of kinetic experiments and kinetic data analysis, organisation of software are also discussed in the paper.

Keywords: automated system for kinetic research

Introduction

Methods of thermal analysis are widely used in reaction kinetic investigations [1]. They provide highly informative data under temperature programmed conditions, enable simultaneous recording of different characteristics of the system and reduction of measurement time. Nevertheless, organization of correct kinetic experiment in non-isothermal conditions and data processing are rather complicated and time-consuming [1]. Besides, kinetic research itself constitutes a sophisticated multi-stage iterative procedure (Fig. 1). Its realization demands application of mathematical methods, numeric simulation, non-linear programming. Consequently, the full performance of the technique is practically impossible to attain without automation of all the stages with regard to their interconnections. Development of an automated system for kinetic research (ASKR) in thermal analysis offers a solution to this problem.

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– increasing the effectiveness of kinetic investigations by means of automation of routine procedures, improving the accuracy and reliability of the results, by excluding non-objective factors as far as possible;

– attainment of a higher quality of results by using more exact methods, impracticable without automation;

– combination of experimental equipment and computer;

– unification of ASKR including its problem-oriented sub-systems for use in the practice of thermoanalytical research.

The structure and the main functions of ASKR, developed in our institute as a result of continuous work for many years [2–5], are presented in this article.

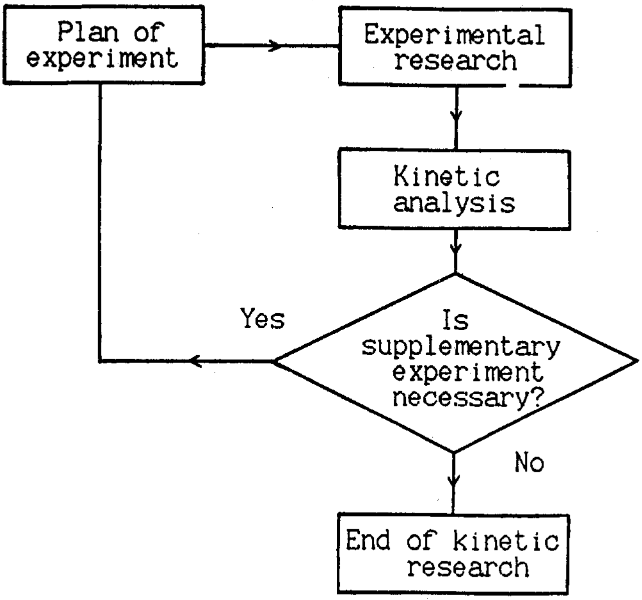

Fig. 1 Kinetic research organization

Purpose and functional structure of ASKR

ASKR comprises a combination of experimental, methodological, calculating and software means. It is developed for the kinetic investigation of chemical processes and synthesis of their mathematical descriptions. The system being discussed is aimed at investigations on heterogeneous reaction kinetics (for instance, gas-solid), interactions in liquid phase and processes of thermal decomposition.

ASKR consists of two functional automated subsystems (AS) – 'THERMOKINETICS' and 'KINETIC ANALYSIS'.

AS 'THERMOKINETICS' aims at an experimental research of chemical processes as a whole and separate stages of processes by means of thermoanalytical methods.

AS 'KINETIC ANALYSIS' aims at constructing mathematical models of chemical processes on the basis of experimental data, obtained by means of AS "THERMOKINETICS".

System 'THERMOKINETICS'

Technical basis of the system

Choice of thermo alanalytical devices is based on the class of objects under examination and the required range of experimental conditions. In accordance with ASKR applications, in AS 'THERMOKINETICS' a complex of thermoanalytical devices 'SETARAM', including microcalorimeter C–80, differential scanning calorimeter DSC–111 and thermoanalyser TG–DSC–111 is used. This complex makes it possible to carry out kinetic investigations of processes with heat evolution and mass change in a wide range of temperatures (170–1000 K), pressures (up to $1.5\cdot 10^7$ Pa) and in various gaseous atmospheres. The set of experimental reactive cells allows to simulate different ways of carrying out chemical processes including forced agitation (in C–80 calorimeter).

For experiment automation IBM–compatible PC AT is used.

Methodological supplement of AS 'THERMOKINETICS'

Correctness of experiment

In kinetic investigations it is essential to ensure a possible uniform distribution of temperature and reagent concentrations in a sample (thermophysical and concentration correctness of experiment [6, 7]). We classified different techniques of carrying out correct experimental and developed experimental and calculating procedures for correctness testing.

Temperature correctness of the experiment

The temperature of the reacting system which is one of the fundamental parameters of the experiment, is not measured directly as a rule. In order to obtain reliable estimation of this quantity we modified the temperature calibration procedure for the calorimeters DSC–111 and C–80 and developed a method of reacting sample temperature calculation according to calorimetric signal measurements. It should be noted that in the TG–DSC–111 device mass loss measurements are carried out simultaneously with calorimetric signal measurements in the same calorimetric cell. That is why temperature estimations obtained are equally related to calorimetric and thermo-gravimetric experiments.

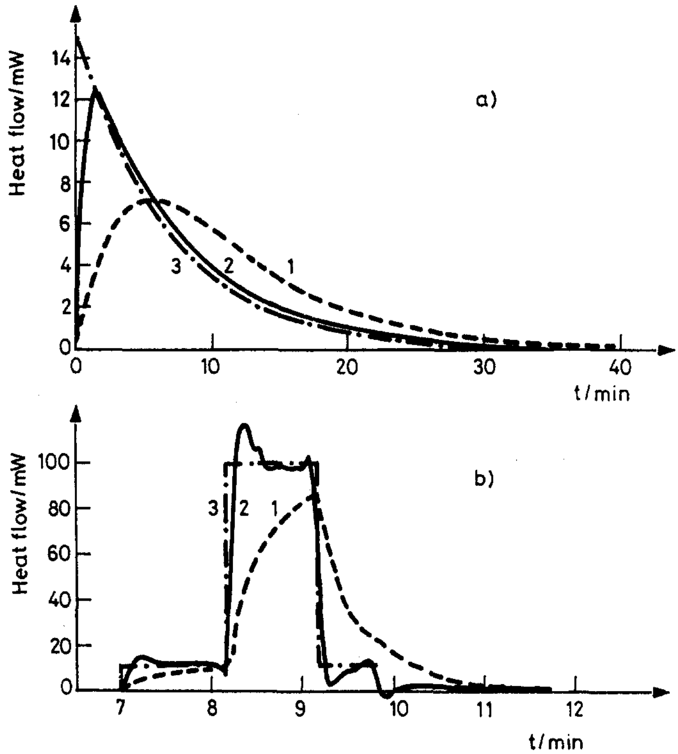

Fig. 2 Deconvolution of calorimetric data.
1 – experimental curve; 2 – deconvoluted curve; 3 – original heat flow; a) C–80, isothermal heating program; b) DSC–111, linear heating program

Nowadays complicated linear-sectional heating programs (combination of constant and linearly changing temperature sections) are widely used. In the moment of going from one temperature section to another the process of temperature gradient re-adjustment takes place in the calorimetric cell. This process may significantly affect the experimental results. Analysis of applicability of complicated heating programs was carried out on the basis of the physical model of a heat flux calorimeter. The conditions, ensuring the correctness of kinetic experiments were also determined.

Calorimetric data deconvolution

A measuring calorimetric cell, because of heat inertia, induces dynamic distortions that lead to significant deformation of kinetic curves in some cases. We have developed the procedure of experimental data deconvolution for their correction [5]. Examples of its application are presented in Fig. 2. Even if the distortions are not considerable, they may lead to considerable errors in the estimation of kinetic model parameters. For example, correction of distortions with an amplitude of 3–5% of the heat evolution rate, diminishes the error of kinetic parameters determination by a factor of two.

Statistical analysis of data

Data error is an important characteristic of any data set. It is determined by a statistical processing of results of parallel experiments. The results of a kinetic experiment have usually the form of kinetic curves, presenting the change of some system property with time. For their statistical processing we have developed a special algorithm based on the probability analysis theory. It allows to estimate data reproducibility quantitatively and to build an average kinetic curve and error corridor [9, 10].

Software for AS 'THERMOKINETICS'

The software for thermokinetic experiment is produced on the basis of methodological developments. It is made as an application package (AP), called 'EXPERIMENT' [11], on IBM compatible computers PC XT/AT. This AP includes program modules 'CONTROL MODULE', 'DATA BASE', 'INITIAL PROCESSING'.

The 'CONTROL MODULE' automates all operations, connected with carrying out the experiments:

- experiment control;
- data collection;
- visual presentation of experimental run by graphics means;
- recording of experimental results into data base;
- producing of static and dynamic DSC-, DTA-calibrations based on Joule effect or on phase transitions in standard substances.

The 'CONTROL MODULE' allows to work with 'SETARAM' devices, controlled by microprocessor controller G–11, or by harware. In the latter case the computer is equipped with a special interface, including multi-channel analog-digital and digital-analog converters, and digital outputs for device units control. This interface provides connection of computer with devices of any specification.

The distinguishing feature of this module is its ability to work in background mode, allowing to use other modules simultaneously with experiment control.

There is possibility to come to active experiment control for testing its running, correcting experimental parameters and so on.

The 'DATA BASE' module serves for storing experimental data, for processing results and data on experimental conditions. The data base control system enables carrying out all necessary procedures like addition, search, looking through, editing and deleting of information.

The 'INITIAL PROCESSING' module is used for obtaining heat evolution rate and mass loss as functions of time according to the signals being measured. The structure of the module and algorithms being applied are synthesized on the basis of informational flowsheet system analysis in AS [9].

The data processing procedure or its separate stages may be performed repeatedly, if necessary. It should be stressed that processing of the full kinetic curve or its separate parts is also possible.

The module performs the following functions:

- numerical data integration and data differentiation;
- correction of the device zero drift;
- base line reconstruction under the 'peak' on different algorithms;
- calorimetric data deconvolution;
- filtration and editing of kinetic curves;
- statistical analysis of data;
- adding or substracting of kinetic curves;
- heat capacity determination;
- data preparation for kinetic analysis.

'KINETIC ANALYSIS' system

Methodological supply of kinetic analysis

Structure of the kinetic models

Mathematical models of chemical reactions in condensed substances are formulated in the form of ordinary differential equations. These models are one- or two-responsed and make it possible to simulate the kinetics of changes of such process characteristics, as heat evolution, mass loss, gas evolution and so on. Any of these characteristics may be presented both in integral and differential form.

For construction of models with complicated structure we have suggested a procedure of automated model synthesis from a standard set of kinetic equations, describing separate stages of a process. There is a common view of the model structure:

$$\frac{\mathrm{d}S}{\mathrm{d}t}=\sum_{i=1}^{w}\sum_{j=1}^{r(i)}\bar{S}_{\mathrm{ij}}\cdot\left(\frac{\mathrm{d}a_{\mathrm{i}}}{\mathrm{d}t}\right)_{\mathrm{j}}$$

$$\frac{\mathrm{d}a_{\mathrm{i}}}{\mathrm{d}t}=\sum_{j=1}^{r(i)}\left(\frac{\mathrm{d}a_{\mathrm{i}}}{\mathrm{d}t}\right)_{\mathrm{j}}$$

$$\left(\frac{\mathrm{d}a_{\mathrm{i}}}{\mathrm{d}t}\right)_{\mathrm{j}}=f_{\mathrm{ij}}\,(\,a_{\mathrm{i}}\,)\cdot K_{\mathrm{ij}}\,;$$

S – response; a – degree of conversion in the i-th reaction; $\left(\frac{\mathrm{d}a_{\mathrm{i}}}{\mathrm{d}t}\right)_{\mathrm{j}}$ – rate of the j-th parallel stage in the i-th reaction; $\bar{S}$ – specific value of property at stage j at $a_{\mathrm{ij}} = 1$; $K = K_o\cdot \exp(-E/RT)$ – rate constant of a stage; $T = T(t)$ – temperature of the reacting system as function of time; w – number of reactions; r – number of parallel stages.

K_o; E; n; m; $\bar{S}$; z – model parameters.

Some functions from a standard set of kinetic equations are also presented:

$$f(a):\begin{cases}(1-a)^n & \text{– N-order reaction}\\[2ex] a^n & \text{– degree reaction}\\[2ex] (1-a)\cdot(a+z) & \text{– simple autocatalysis}\\[2ex] a^n\cdot(1-a)^m & \text{– autocatalytic reaction}\\[2ex] (1-a)\cdot(-\ln(1-a))^n & \begin{array}{l}\text{– solid-state reaction}\\ \text{(Avramy–Erofeev model)}\end{array}\end{cases}$$

Multistage independent, parallel reactions and their combinations can be described by means of various combinations of basic equations.

It must be mentioned that the proposed procedure makes it possible to synthesize all types of kinetic models widely used in thermal analysis.

Initial data for kinetic analysis

Structural and parametric identification is carried out during the inverse task solving on the basis of experimental data after initial processing.

Data may be heterogeneous:

– kinetic curves, representing changes of any reacting system responses or rates of response changes in time (integral of differential form);

- sets of response values corresponding to parallel runs;
- observations omitted.

The possibility of simultaneous use of experimental data obtained in different temperature-temporary modes is the unique peculiarity of the system.

Task definition

The requirements for correct inverse taks definition are their mathematical definiteness and physical determinancy [12]. Mathematical definiteness denotes existence and single-value of inverse task solution for an arbitrary set of experimental data. Physical determinancy means solution stability by small data variations.

Inverse tasks in thermal analysis are usually not correct from the mathematical point of view. The solution existence is guaranteed if the number of model parameters is a finite quantity and their determination region is defined. But further analysis is required for determination of solution single-value of stability. In practice the conclusion about the task definition correctness may be made only after finding out point estimation of the parameter vector P and its analysis.

Parametric identification

Parametric identification consists in the parameter evaluation of a given kinetic reaction model. The methodology of parametric identification is based on the least squares methos (LSM) [13]. LSM does not require the knowledge of the distribution law of observations and is suitable for realization on computers. This method is useful for heterogeneous experimental data processing and permits to determine not only kinetic parameter sets (activation energy, pre-exponential factor, reaction order and so on) but also such factors as the initial values of conversion degree, concentrations etc. In case of non-linear models the LSM realisation is based on the application of non-linear programming methods [14].

There is no universal method which is equally effective in various cases. Therefore a set of different methods is used in practice. Based on our experience we have chosen the Gauss–Newton method (numerical realisation [15]), giving the best results for the models mentioned above. The main idea of this method is linearization of the determined component $f(P)$ of the observation model:

$$y = f(P) + e$$

where y – is the reacting system response, e – experimental error.

Examples of kinetic model parametric identification are presented in Fig. 3.

Single value and stability of solution

The causes of solution multi-value are the model structure, deficiency of experimental data and their error. Cases of global and local multi-value are distinct [16].

No general mathematical method is available for diagnosing solution global multi-value, therefore the corresponding verification is made in our software by means of calculation experiment.

We applied [17] the method of weighted Jacoby matrix singular analysis [18] for a posteriori determination of local multi-value. This method allows also to determine the degree of solution stability to small experimental data variations.

The experimental data set or model structure in case of infringement of the correctness conditions has to be reviewed.

Problem of adequateness

Adequateness means the equivalence between experimental data and kinetic description while using a model and is determined by means of residual analysis.

Adequateness verification is a key moment of stastistical analysis and is worked out after determination of single-value and stable model parameter estimation. As very often no information is available about the error distribution we propose to use the following formal criterion:

$$\text{abs}\ (y - f(P)) > Em,$$

where Em is vector of experimental error estimation given by the investigator.

This expression means that the absolute error of data description (value of residuals) must not exeed the experimental error estimation. This criterion has a predictive nature and is suitable in the absence of parallel runs for single- and multi-response models. But complete adequateness problem solution may be found only by taking into consideration the entire set of qualitative and quantitative data.

Error of parameter estimation

Parameter estimation error may be determined using probability methods [13] or the Bayes approach [19]. But correct solution of this problem is possible only by means of robust methods [20] as the distribution law of observation errors is usually unknown. We propose to use the envelope surface of permissible parameter value region D for robust error characteristics:

$$D = \{P\ |\text{abs}\ (f(P) - y) < Em\ \}.$$

Region D may have large dimesions and complex configuration because of the correlation between parameter estimations. But its two-dimension cross-sections allow to predict the error.

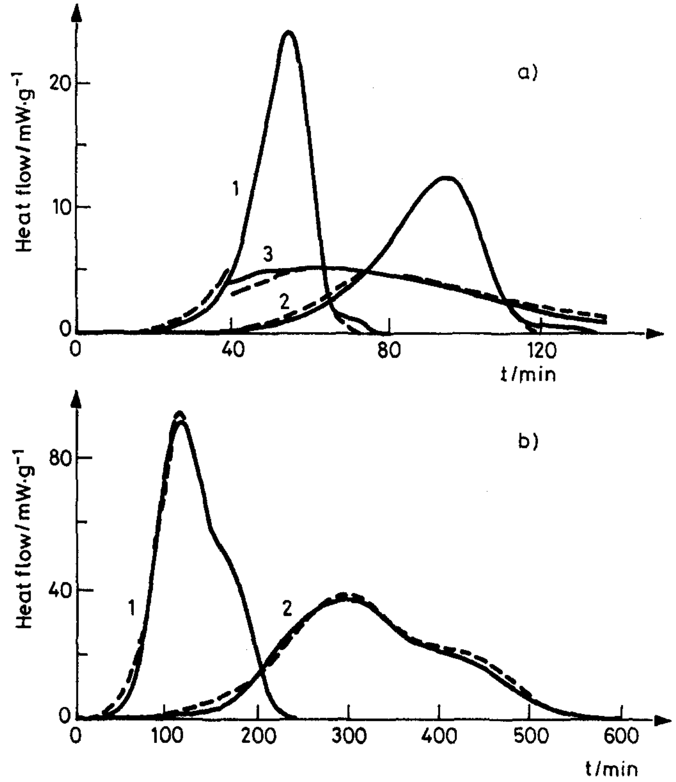

Fig. 3 Parametric identification.
—— experimental curves; — — — results of kinetic analysis 1,2 – linear heating program; 3 – isothermal part of combined heating program.
a) Thermal decomposition of 2, 4, 6 – Trinitrophenyl-methyl-nitramid.
Model of full autocatalysis:
$dQ/dt = \bar{Q}_1 \cdot (da/dt)_1 + \bar{Q}_2 \cdot (da/dt)_2$
$(da/dt)_1 = K_1 \cdot (1-a)^{n1}$; $(da/dt)_2 = K_2 \cdot a^{n2} \cdot (1-a)^{n3}$
b) Liquid- phase reaction: 1,2 – dichlorethane + ethylendiamine
Model of sequential reactions:
$dQ/dt = \bar{Q}_1 \cdot (da_1/dt) + \bar{Q}_2 \cdot (dQ_2/dt)$
$(da_1/dt) = K_1 \cdot (1-a_1)^{n1}$; $(da_2/dt) = K_2 \cdot (a_1 - a_2)^{n2}$

Structural identification

Definition of kinetic model structure is the stage which is the most difficult to formalize. It is executed by discrimination of kinetic models from some ensemble through comparing their prognostic ability in distinctive conditions. Both a priori and a posteriori information is widely used for this purpose.

Software for AS 'KINETIC ANALYSIS'

Functions of AS 'KINETIC ANALYSIS' are realized in the application package 'MACROKINETICS' on IBM compatible computer PC AT. PP consists of the following program modules;

- 'DATA BASE';
- 'DIRECT TASK';
- 'KINETIC ANALYSIS'.

The 'DATA BASE' module is used for storing of experimental data, kinetic models and parameter sets and provides all necessary procedures connected with adding, search, looking through, editing and deleting of information. Information may be united according to some indicator (substance, name, chemical reaction, process, et.).

The 'DIRECT TASK' module is used for calculating the response of the reacting system according to known kinetic reaction description and reaction conditions in the absence of concentration and temperature gradients. Calculations are made analytically or by one of the standard numerical integration methods.

Chemical reaction kinetic description corresponding to experimental data is obtained by means of the 'KINETIC ANALYSIS' module.

The module makes possible:

- to take single-value and stable inverse task solution;
- to estimate all or only part of the kinetic model parameters;
- to determine parameter estimation error;
- to estimate the adequateness between experimental data and kinetic description;
- to carry out computational experiment.

Estimation of ASKR metrological characteristics

One of the significant problems connected with the use of ASKR is the estimation of the metrological characteristics of the system as a whole and of its subsystems. The method of error estimation by means of standards is widely used in thermal analysis. But this method cannot be applied in kinetic research because of the absence of standard reacting systems, wide range of the physical-chemical properties of the reagents and the great variety of reaction conditions.

We have worked out the method of simulating experiment [21], which can be regarded as a possible solution to this problem in calorimetric research.

Simulating experiment is a procedure which makes it possible to realize in the DSC cell the heat process with given heat evolution program under conditions as close to experimental ones as possible. The heat evolving element in such experiments is a microheater inserted in the experimental cell or standard calibration cell included in the set of heat flow calorimeters.

Simulation of the desired heat evolution program is ensured using computer-controlled power supply of the microheater. The temperature dependence of heater resistance is taken into account automatically in non-isothermal conditions.

There are two ways of simulating thermophysical conditions. The first way is to insert the heater into the cell containing inert substance having similar thermophysical properties to those of the substance under investigation. Another way is to insert the heater into the cell containing the real sample. But simulating experiment is carried out in this case in a temperature region where chemical transformations are absent.

Metrological characteristics are estimated by comparison of data processing results and known parameters of the thermal process.

In calorimetric research simulating experiments allow:

- to carry out static and dynamic calibration of the calorimeter;
- to estimate the correctness of algorithms used for processing of experimental data;
- to estimate the errors of the determination of heat evolution rate and heat effect;
- to estimate experiment reproducibility.

Simulating experiments in kinetic research make possible:

- to simulate the heat evolution corresponding to the required kinetic law;
- to estimate the metrological characteristics of a kinetic experiment;
- to estimate the influence of experimental errors on the accuracy of kinetic parameters determined by kinetic analysis of the data of the simulating experiment without model error.

It must be pointed out that AS 'KINETIC ANALYSIS' allows to execute a computing experiment which also may be used for AS self-testing. Such an experiment is often useful for the design of additional or control runs during kinetic research.

Organization of ASKR software

The software works in MS DOS operation system (version 3.3 and higher). Programming languages 'C', 'FORTAN' and 'ASSEMBLER' were applied for software creation.

The software makes possible to use all its features without special knowledge in programming, computational mathematics of mathematical methods of chemical kinetics.

The interactive mode of the package simplifies greatly its use without universal instruction demands. Moreover, this mode gives the opportunity to unite the formalized methods of process description with researcher experience and intuition, allowing him to influence the problem solving.

The interactive mode of the packages is created using the 'menu' type ierarchical principle. All the questions included in the 'menu', are provided with replies, where necessary. The interactive mode makes possible to accomplish syntax and context control, if necessary. The researcher may use 'help' when difficulties arise.

The application of graphical means provides all obvious ways of information presentation, facilitates the anlysis of results and makes easier to draw conclusions.

The data bases of application packages are fully compatible, so the packages may be applied using both one- and two-level ASKR computer facility. In the latter case the informational connection between computers is provided easily by means of diskette.

It must be pointed out that application packages may be used in complex or independently.

The software created has a full set of documentation including owner's manual and recommendations concerning kinetic research carried out in ASKR. All this facilitates the use of our software in the practice of thermoanalytical research.

Conclusion

The experience accumulated on ASKR operation in our institute confirmed completely the usefulness of such system development and its effectiveness in respect of reducing the time needed for research and ensuring high quality and reliable results.

ASKR is an open system and allows to expand its possibilities. So a subsystem is now being worked out for the experimental determination of substance characteristics like heat conductivity, degree of purity and some others. A methodology and software are under development for kinetic analysis using kinetic models which are presented in the form of differential equation systems in respect of reagents concentrations. Such profound models are useful for detailed description of complex chemical processes.

It must be noted that the synthesis of reaction kinetic description is not the only purpose. Such description is needed for simulation of various technological reactors, safety analysis of storing and processing conditions of substances with respect to thermal explosion and so on. Therefore ASKR may be used as a subsystem in automated systems of technological process development, safety research etc [4].

* * *

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Zusammenfassung — Kinetische Untersuchungen unter Anwendung thermoanalytischer Methoden umfassen ein kompliziertes, mehrstufiges Vorgehen, deren vollständige Durch-führung ohne Automatisierung aller Stufen in Beziehung auf deren Wechselwirkungen unmöglich ist. Die Entwicklung eines automatisierten Systemes für kinetische Untersuchungen (ASKR) in der Thermoanalyse ist die Lösung des Problemes.
ASKR basiert auf einem Komplex thermoanalytischer Geräte der "SETARAM" Company. Dieses System erlaubt eine Herabsetzung der Messungszeit und sichert qualitativ hochwertige und zuverlässige Ergebnisse.
Aufbau, Zweck und Möglichkeiten von ASKR werden bedacht und es werden auch method-ische Fragen kinetischer Experimente und der Analyse kinetischer Daten sowie Softwareor-ganisation besprochen.