Dedicated to Prof. Dr. H. J. Seifert on the occasion of his 60th birthday

EVALUATION OF THERMAL ANALYSIS EXPERIMENTAL DATA
I. Computer modelling and interpretation of thermal decomposition of solids studied by evolved gas analysis and thermogravimetry

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The possibilities of the THERMOKIN software package for evaluation of experimental data of solid state thermal decomposition are described. The software package makes it possible to simulate the solid state reactions, to evaluate the results of various thermal analysis methods such as TG/DTG, DSC, evolved gas analysis etc. The software enabled us to choose the adequate model of solid state reactions, to calculate the parameters of reactions and the errors of the parameters. Using this software package the interpretation of the results obtained by various methods of thermal analysis as well as the determination of the optimal experimental conditions for the studied substances can be made.

The computer software for mathematical modelling of solid state reactions, and for evaluation of experimental data of various thermoanalytical methods represents an important part of modern thermal analysis.

There are several reasons for the need of computers in modern thermal analysis, namely:

1. The increased information about studied solid state processes;

2. The control of thermal analysis equipment (heating, cooling, flow rate of the gas etc.);

3. The thermal analysis of composites, mixtures, natural rocks and other materials as well as multistage solid state processes accompanied by phase

transitions and chemical reactions make mathematical description rather complicated, which can be solved by means of powerful computers.

In this paper the principles of the computer software package THERMOKIN are described. The THERMOKIN software package can be used for optimization and planning of experiments, for the simulation of various mechanisms of solid state reactions as well as for evaluation and interpretation of results of several thermal analysis methods. The main attention will be paid to the decomposition reactions of solids accompanied by gas evolution, i e. the cases where thermogravimetry and evolved gas analysis are appropriate methods of application.

Purpose and structure of THERMOKIN computer software package

1. To simulate solid state reactions under isothermal and non-isothermal conditions using analytical, numerical and statistical methods.

2. To evaluate the results of TG/DTG, DSC, EGA, emanation thermal analysis, dilatometry and other methods.

3. To calculate the solid state reaction parameters and their errors of determination.

4. To interpret the results of several methods with the aim to determine the mechanism of the solid state processes.

5. To store the experimental data in the data base.

6. To plan and optimize the experiments.

The solid state reaction mathematical model bank consists of analytical and numerical solutions of the thermal analysis problems. In the data base the concise descriptions of the thermoanalytical curves, experimental conditions, calculated thermodynamical and kinetic parameters of solid-state processes and their errors are stored.

The THERMOKIN computer software package is applicable for IBM PC or compatible computers.

Methods of analysis of the kinetic curve form

1. Functional scale

Let us consider the construction of functional scale for the case of gaseous products release in the linear heating regime: $T = T_0 + \beta t$ (diffusion

resistance is neglected). The reaction of thermal decomposition is formally described by the first order kinetics.

As it is known [1], the dependence of a gas flow, J, on time, t, (or temperature, T) in the first order solid state reaction is described by the equation:

$$J(T) = k_0 \cdot a_0 \cdot \exp(-E/RT) \cdot \exp(\tau) \tag{1}$$

where

$$\tau = \frac{k_0 E}{\beta R}\left[-\frac{\exp(z)}{z} + Ei(z)\right] \quad \text{for the limits} \quad \left|\begin{array}{l} z = -E/RT \\ z = -E/RT_0 \end{array}\right.$$

and $Ei(z) = \int_{-\infty}^{z} \frac{\exp(t)}{t}\, dt$ — integral– exponential function; k_0 is pre-exponential factor, a_0 is initial fraction of reagent, R is the gas constant, β is the heating rate T_0 is the temperature of the onset of sample heating, T is the current temperature.

The time dependence of the gas flux $J(T)$ can be represented by an asymmetric peak-like curve with the temperature maximum (T_m) defined by solving the transcendent equation

$$\ln(k_0/\beta) - \ln(E/R) + 2\ln T_m - E/RT_m = 0 \tag{2}$$

To construct the functional scale Eq. (1) we can write

$$F(U) = F\left(\frac{E}{RT} - \frac{E}{RT_m}\right) = \frac{J(T)}{J(T_m)} = \exp\left[-\left(\frac{E}{RT} - \frac{E}{RT_m}\right)\right]$$

$$\cdot \exp\left\{-\frac{k_0}{\beta}\left[\frac{RT}{E}\cdot\exp\left(-\frac{E}{RT}\right) - \frac{RT_m}{E}\cdot\exp\left(-\frac{E}{RT_m}\right) - \right.\right.$$

$$\left.\left. - Ei\left(-\frac{E}{RT}\right) + Ei\left(-\frac{E}{RT_m}\right)\right]\right\} \tag{3}$$

Dividing the variation range (0–1) of function $F(U)$ into several intervals we can calculate the values U corresponding to the values $F(U)$. The functional scale is plotted on the ordinate axis: the value of U is marked to the right of the axis in the usual scale and to the left- the corresponding

values of $F(U)$ in the functional scale. The values $1/T$ (K^{-1}) are given on the abscissa axis.

In the case that experimental or model curve is well described by the first order kinetics, after reconstructing it in a given functional scale, the straight line appears on the $F(U)$ graph which is described by the equation

$$U = E/RT - E/RT_m = E/RT - \ln(k_o RT_m^2/E\beta) \qquad (4)$$

The activation energy $E = R_o \, \text{tg} \, \gamma$ was determined from the curve slope (tangent) and the pre-exponential factor k_o — from the segment cut off on the ordinate axis. In the form of the EGA curve does not obey the first order kinetics, then the graph of the curve plotted in the functional scale deviates from the straightforward line dependence. One can judge on the mechanism of the solid state process according to the deviation character of the obtained graph.

2. The temperature dependence of the effective activation energy of the gas release

When analysing the thermostimulated gas release spectra an essential problem is to elucidate the question: is there only one solid process or are there several processes, i.e. is it possible to describe the gas release curve using a single activation energy or it is necessary to resort to a concept of the activation energy spectrum [3, 4]. The analyse poorly resolved DTG curves one may use the temperature dependence of effective energy of thermostimulated gas release, $E_{ef}(T)$. The values of the effective kinetic constant of gas release are calculated at every point on the experimental curve:

$$k_{eff} = \frac{J(T)}{\alpha(T)} = \frac{J(T)/A}{1 - A\int\limits_{T_o}^{T} J(T)\,dT} \qquad (5)$$

Here $A = \int\limits_{T_o}^{T_f} J(T)\,dT$ is the area of the EGA or DTG peak, T_o and T_f are the onset and final temperature of the heating respectively. The $1/T$ dependence of $\ln(k_{eff})$ is plotted and the values of the effective activation energy, $E_{eff}(T)$ and the pre-exponential factor $k_{oeff}(T)$ are calculated at each point of the obtained curve. The 'elementarity' of the DTG curves can

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be judged from the form of the obtained dependences. In the case when the process is described by the activation energy only, the $E_{eff}(T)$ graph will be linear and parallel to the abscissa axis. When the activation energy spectrum is presented the $E_{eff}(T)$ graph just as $k_{oeff}(T)$ graph will be descending function. As the resolution improves, explicit plateau appears on the $E_{eff}(T)$ graph which reflects the extreme energy values in the solid state process spectrum.

For instance, if the release process is characterized by two activation energies, E_1 and E_2 with contribution φ_1 and φ_2 respectively, ($\varphi_1 + \varphi_2 = 1$), then the expression for the slope tangent of the curve plotted in coordinates $\ln(k_{eff}) - 1/T$ for every point is of the form

$$\frac{\partial \ln(k_{eff})}{\partial 1/T} = -\frac{E_1 \varphi_1 J_1 - E_2 \varphi_2 J_2}{R(\varphi_1 J_1 + \varphi_2 J_2)} + \frac{T^2[\varphi_1 J_1(k_1 - k_{eff}) - \varphi_2 J_2(k_{eff} - k_2)]}{\beta(\varphi_1 J_1 + \varphi_2 J_2)}$$
(6)

If the EGA or DTG curve lines are not too overlapped (i.e. $\Delta E = E_2 - E_1$ is large enough) than at the beginning of curve $J_2 \to 0$ and

$$\frac{\partial \ln(k_{eff})}{\partial 1/T} = -\frac{E_1}{R} + \frac{T^2}{\beta}(k_1 - k_{eff})$$
(7)

Since $(k_1 - k_{eff}) \to 0$, then exp. (7) gives initial estimate of E_1. It is also seen from (7) that the presence of other lines in the spectrum of the solid state process of thermal decomposition lead to an absolute value decrease of the effective activation energy at beginning of curve. As the decomposition proceeds, $J_1 \to 0$ and

$$\frac{\partial \ln(k_{eff})}{\partial 1/T} = -\frac{E_2}{R}$$
(8)

i. e. at high temperature E_{ef} increases and tends to $E_{eff} = E_2 > E_1$ provided potential wells with E_1 are empty.

Thus at beginning of curve E_{eff} is equal E_1 then drops afterwards, increases again during heating and reaches E_2 provided the gas release flux is determined already by the second line only. ✽

3. The compensation effect

When describing the temperature dependence of the rate constant of a gaseous product release it is usually supposed that the parameters k_0 and E are mutually independent. However, in several cases a dependence does exist. It may appear when effective values of k_0 and E are used for processing of gas release curves at multiple form of the activation energy spectrum. The gas release curve with one activation energy is presented on the $\ln(k_{eff})-1/T$ graph as a point, for the nonresolved EGA peak – as a monotonous curve growing to a value corresponding to the minimum energy of spectrum and at a good resolution of spectrum – as monotonous curves coming from one point and growing to values corresponding to extreme lines of energetic spectrum. The form of compensation effect curves may be used to identify the fine structure of EGA curves.

4. Statistical moment method

In the moment method the EGA peak normalized to its area is considered formally as a density distribution function of some random quantity, $J(T)$. Then proceeding from the measured gas release curves under linear heating stage, $J(T)$, the initial moments are found [5]

$$\mu_k = \int_0^\infty J(\tau) \cdot \tau^k \, d\tau \qquad (9)$$

then — the central moments

$$M_1 = 0 \qquad (10a)$$

$$M_2 = \mu_1 - \mu_2^2 \qquad (10b)$$

$$M_3 = \mu_3 - 3\mu_1\mu_2 + 2\mu_1^3 \qquad (10c)$$

$$M_4 = \mu_4 - 4\mu_1\mu_3 + 6\mu_1^2\mu_2 - 3\mu_1^4 \qquad (10d)$$

and finally the principal moments (the asymmetry and excess factors)

$$\beta_1 = M_3/M_2^{3/2} \qquad (11a)$$

$$\beta_2 = M_4/M_2^2 \qquad (11b)$$

Plotting the dependences graph $\beta_1 - \beta_2$ one can get some card (analogous to the Pirson card) where solid state reactions with various mechanism are presented as points, curves or regions.

Solid state process modelling

The THERMOKIN computer software package makes it possible to simulate a solid state process by two methods: using a formal kinetic approach and using a statistical method.

Modelling with a formal kinetic approach

As it is known the thermal analysis is used to study various types of solid state processes. These are thermal decomposition reactions, solid state reactions in powder mixtures, gas-solid interactions or liquid-solid interactions etc. In the THERMOKIN bank of mathematical formal kinetics models is based on solving usual differential equations and equations of particular derivatives allowing to compute changes of amount of newly produced phase in time, thermal effects, the release of volatile products as well as changes of linear dimensions and specific surface of the sample investigated. Linear differential equations are solved by analytical methods and nonlinear differential equations - by numerical methods.

In the framework of the formal kinetic approach it was assumed that the rate of the solid state process can be written as

$$-\frac{d\alpha}{dt} = kf(\alpha) \qquad (12)$$

where k is rate constant of solid state reactions, α is reaction degree.

Different methods of writing function $f(\alpha)$ exist, we use the most common [6]:

$$f(\alpha) = \alpha^m (1-\alpha)^n [-\ln(1-\alpha)]^p \qquad (13)$$

where specific values of the constants m, n and p defined by the development character of a solid state process in the space and time: random char-

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acter of new phase creation in the sample volume, nucleation and growth of nuclei, formation of nuclei on the surface of a sample or on the boundaries of grains etc.

For example, for kinetics of a contracting sphere (Jander model):

$$-\frac{d\alpha}{dt} = k_3 (1 - \alpha)^{2/3} \tag{14}$$

for the chain process mechanism with a break of chains (Prout–Thomkins model):

$$-\frac{d\alpha}{dt} = k_{PT} \alpha (1 - \alpha) \tag{15}$$

In the linear heating regime including the temperature dependence of the reaction rate constant

$$-\frac{d\alpha}{dt} = \frac{k_0}{\beta} e^{-E/RT} f(\alpha) \tag{16}$$

where E is the activation energy of a solid state process or

$$\ln \left(\frac{d\alpha}{dT} \cdot \frac{1}{f(\alpha)} \right) = \ln (k_0/\beta) - E/RT \tag{17}$$

A serious problem is the transition from the reaction degree α to the "experimental" curves: TG/DTG, DSC, EGA etc. In the rough approximation it may be assumed that the observed experimental effects are proportional to the reaction degree α. However, the methods of statistical modelling of solid state process development in space and time demonstrate the complicated relationships between registered effect and the reaction degree α, that complicates the task to find $f(\alpha)$ from the thermal analysis experiment data.

In addition to mathematical expressions which describe the formal kinetics of a solid state reaction the THERMOKIN model bank contains differential equations in particular derivatives, which numerical solution makes it possible to simulate such processes as

1) water release from porous bodies taking into account inhomogeneous moisture distribution, the existence of the temperature gradient and the

phase transformation (i.e. supposing different relations between evaporation and condensation);

2) nonisothermal kinetics of sorption taking into account thermal effects of adsorbat–adsorbent interaction;

3) diffusion of reacting in the catalyst layer etc.

The THERMOKIN software provides the modelling of chemical reaction accompanied by thermal effects (temperature distribution in reaction volume is described by a system of equations for Fick and Fourier laws based in the chemical reaction kinetics). The mass and enthalpy balances may be represented as

$$\frac{dc}{dt} = D_e \left(\frac{\partial^2 c}{\partial r^2} + \frac{a}{r} \frac{\partial c}{\partial r} \right) - k(T) f(\alpha)$$

$$\rho \, c_P \frac{dT}{dt} = \lambda_e \left(\frac{\partial^2 T}{\partial r^2} + \frac{a}{r} \frac{\partial T}{\partial r} \right) + q^* k(T) f(\alpha) \tag{18}$$

where D_e is the effective coefficient of diffusion, $k(T) = k_0 \exp(-E/RT)$ is the temperature dependence of the reaction rate constant, ρ is the matter density, c_p is specific heat capacity, λ_e is the effective coefficient of heat conductivity, q is the reaction heat, a is parameter of the grain form ($a = 0$, 1, 2 – for a plate, cylinder and sphere respectively). $f(\alpha)$ is the chemical kinetics law, e.g. $f(\alpha) = c^n$. Here the initial conditions are: $c(r, 0) = c_0(r)$, $T(r, 0) = T_0(r)$. The boundary conditions take into account the influence of mass- and heat transfer from surrounding matter to the surface of a particle:

$t > 0$

$$r = r_0; \qquad c = c_e - \frac{D_e}{\alpha_c} \frac{dc}{dr}; \qquad T = T_e - \frac{\lambda_c}{\alpha_T} \frac{dT}{dr};$$

$$r = 0; \qquad \frac{dc}{dr} = 0; \qquad \frac{dT}{dr} = 0. \tag{19}$$

where the index e implies the concentration and temperature in the flux washing away the particle of matter, α_c and α_T the coefficients of the mass- and heat–exchange, respectively, r_0 is the characteristic dimension of a powder grain.

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It should be emphasized that the equation system (18) may have more than one solution (three, as usual) depending on the parameter values contained in it. When there are three stationary solutions (multiplicity of states) some of them may be of unstable character. A consequence of this is the possibility of → temperature gradients → in the stationary state, appearance of the autovibrational regime of mass and heat transfer processes in a solid state particle.

Let us briefly mention several examples for models.

Example 1.

Let us consider the thermal decomposition reaction of the n-th order. For the case of absence of diffusion resistance:

$$T \frac{d\alpha}{dt} = k \, \alpha^n \tag{20}$$

The dependence of the gas release flux, J, on the temperature T under linear heating conditions at an Arrhenius type dependence of the coefficient k

$$J(T) = -\frac{d\alpha}{dt} = k_0 \cdot \exp(-E/RT) \cdot \alpha^n \tag{21}$$

where n is the formal order of reaction (as a rule $0 < n < 3$). For the reaction order $n = 1$ the flux calculated from Eq. (21) may be written as Eq. (1). For the reaction order $n \neq 1$ the expression for the flux is of the form:

$$J(T) = k_0 \cdot \exp(-E/RT) \cdot \left(\alpha_0^{1-n} + (1-n) \cdot \tau \right)^{n/(1-n)} \tag{22}$$

Figure 1 shows the influence of n on the position and on the form of DTG curve. The curves normalized to the height of the maximum are given in Fig. 1a in initial scale and in the functional scale they are given in Fig. 1b. It is seen that at low temperatures (the ascending part of the DTG curve) the slope tangent of the straight line part is n independent. The high-temperature (descending) branch of the peak is very sensitive to the order of reaction. For the order $n > 1$ the slope tangent of the graph is smaller while for $n < 1$ is larger than for the first order kinetics. Thus one can always find on the DTG peak a part from which one may calculate the activation energy of reaction independently of formal order and at the same time ex-

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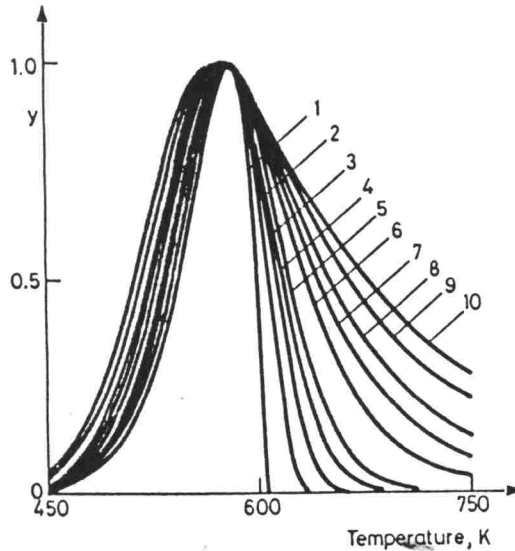hus one can always
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tract a part optimal for determining *n*. Figure 2 shows analogous situation
with the integral curves of weight loss (TG).

Example 2.

Fig. 1a Influence of the chemical kinetics equation order on the form of the gas release
differential curve in the linear heating regime [2].
a) the curves are normalized to their own height; The following orders *n* are considered
in curves 1-10, respectively: *n* = 0.5, 0.8, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5

Let a few parallel independent first order chemical reaction occur in a
sample, each of these reactions being characterized by its value of the
parameters E_i, k_{oi} and by the contribution into total process φ_i [3]. For the
case of discrete energetic spectrum of a solid state process the total flux of
gaseous products from a sample is determined by the equation:

$$J(T) = \sum_{i=1}^{n} \varphi_i \cdot J_i(T) \qquad (23)$$

where φ_i is the contribution of flux J_i if the *i*-th reaction product.

Let us consider as an example a process consisting of two parallel reac-
tions featured by the energies E_1 and E_2 and equal contributions $\varphi_1 = \varphi_2$. In
the course of calculation at a fixed smaller activation energy E_1 the value of
E_2 was increased and resulting curves of gaseous product release were ob-
tained (DTG or $J(T)$ curves). At a few percent difference in energies the

"experimental" curve $J(T)$ (Fig. 3) is a completely nonresolved single peak without a sign of presence of two activation energies (excluding the fact that the peak became more symmetrical). On this account the use of standard resolution criteria (e.g. Rayley criterion) is in this case impossible. The application of the above described methods made it possible to reveal the complex activation energy spectrum.

For instance, calculations of the $E_{eff}(T)$ (Fig. 4) dependences for the DTG curve obtained for the spectrum from Fig. 3, showed that the presence of two activation energies differing only by 1% is already seen on the $E_{eff}(T)$ diagram as a descending function. The minimal activation energy is here determined sufficiently reliably while E_2 is evidently underestimated. At a $\Delta E = 4\%$ difference the multiplicity is fixed exactly as a minimum on the $E_{eff}(T)$ curve through the DTG curve looks like a single peak. The E_1 energy is determined reliably while E_2 with a large error. The 10% energy difference leads to a good resolution of the DTG-curve on the $E_{eff}(T)$ graph. The $J(T)$ reveals the first sign of resolution – a small dip. Both the values of
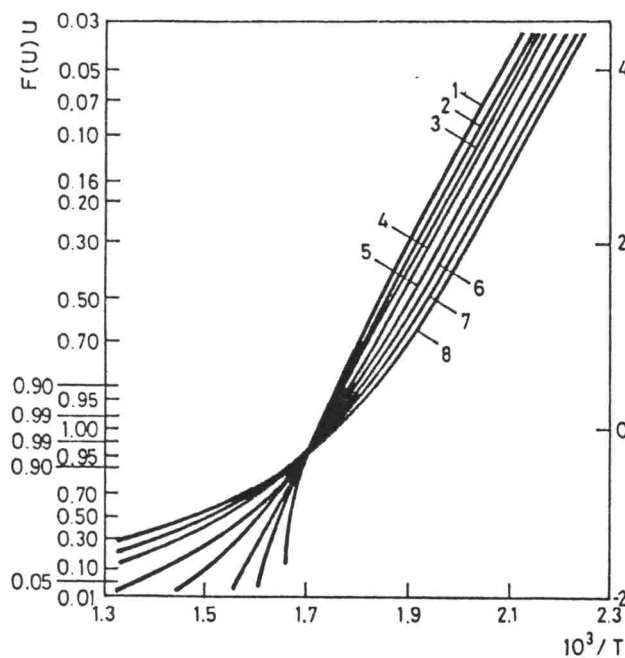

Fig. 1b Influence of the chemical kinetics equation order on the form of the gas release differential curve in the linear heating regime [2].

b) the curves are represented in the functional scale calculated for 1-st order kinetics. The following orders n are considered, curves 1-8, respectively: $n = 0.5, 0.8, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5$

E_1 and of E_2 are determined with an equal degree of reliability. Thus the E_{eff} calculation gives a correct value of the activation energy at the DTG curve points where the gas release flux is determined mainly by one of the lines, i.e. on the edges of this spectrum. The use of 'particular' points or of
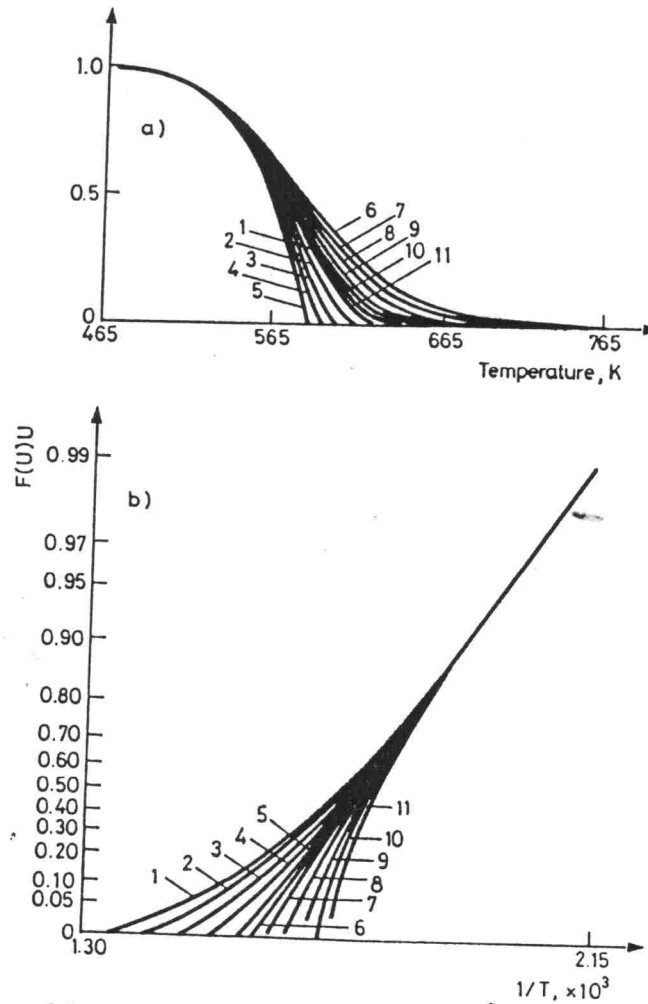

Fig. 2 Influence of the chemical kinetics equation order on the form of the weight loss integral curves (TG) in the linear heating regime [2].
a) the curves in the initial scale; b) the curves in the first order kinetics functional scale
The following orders n are considered in curves 1-11, respectively: n = 0.1, 0.3, 0.5, 0.7, 0.9, 1.0, 1.1, 1.3, 1.5, 1.7, 1.9

the other known interpretation methods of DTG curves to find the E_1 and E_2 values at such low values of E is impossible.

The E_{eff} dependence of ln (k_{oeff}) (compensation effect) are plotted in Fig. 5 for the same spectra. This diagram shows the complicated form of the
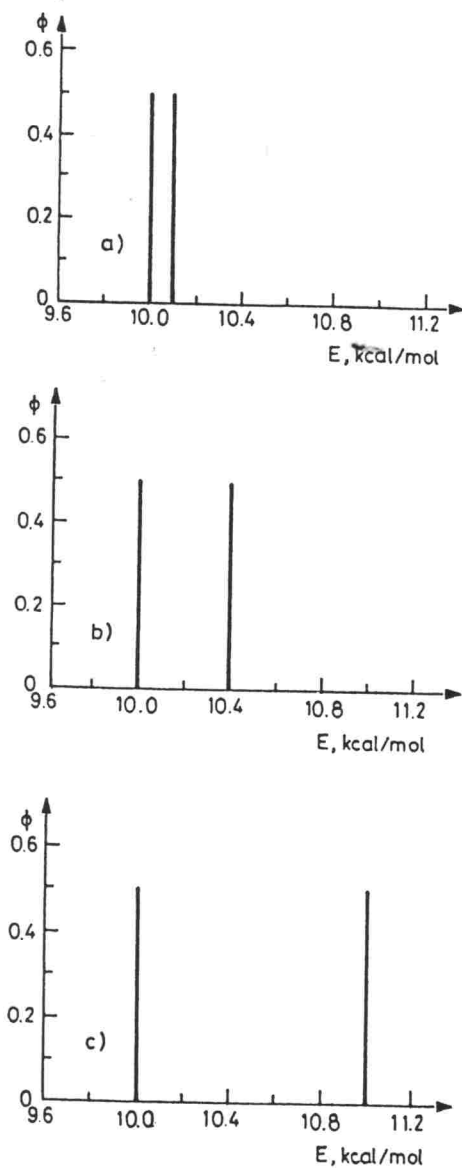

Fig. 3 Discrete energetic spectra of two parallel chemical reactions in the solid with equal contribution ($\varphi_1 = \varphi_2 = 0.5$); a) $E_1 = 10.0$ kcal/mol, $E_2 = 10.1$ kcal/mol b) $E_1 = 10.0$ kcal/mol, $E_2 = 10.4$ kcal/mol; c) $E_1 = 10.0$ kcal/mol, $E_2 = 11.0$ kcal/mol

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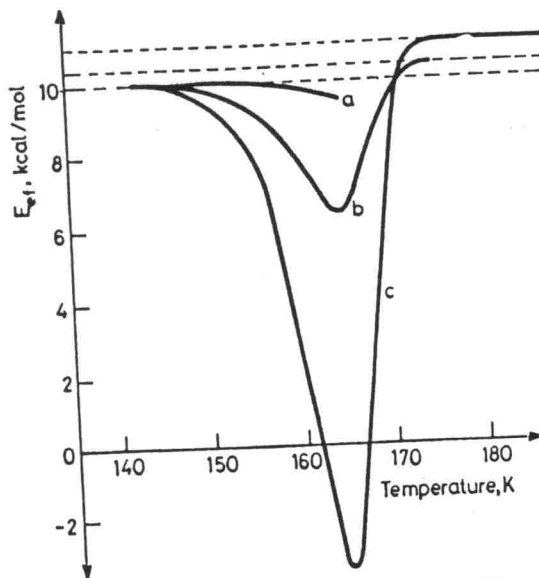
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Fig. 4 Temperature dependence of the effective activation energy, E_{eff}, calculated at each point of the gas release curve from a sample where two parallel first order reaction of the thermal decomposition with discrete spectra from Fig. 3 occur
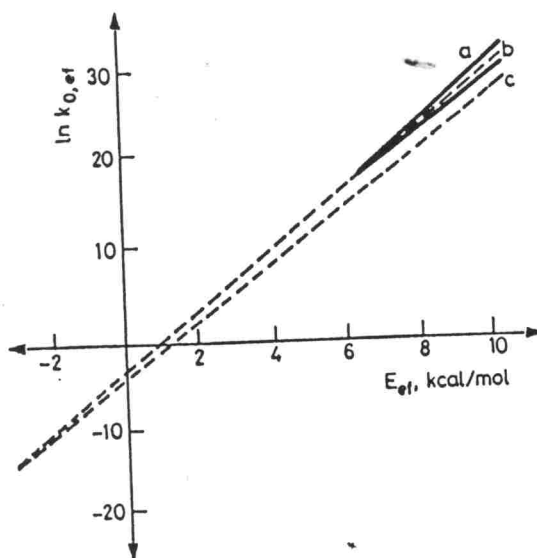

Fig. 5 Plot of the formal dependence of the value $\ln(k_{0eff})$ on reaction effective activation energy, E_{eff}, calculated at each point of the gas release curve from a sample where two parallel first order reaction of the thermal decomposition with discrete spectra from Fig. 4 occur

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nol, $E_2 = 11.0$ kcal/mol

activation energy spectrum at a few percent difference in energies. As for the standard Rayley criterion resolution (the value of flux at the minimum between peaks must be by $e = 2.71$ times smaller than one at the peak maxima), it requires the several dozens percent difference in energies. The formal correlations between the parameters k_{oeff} and E_{eff} is seen from the graph of Fig. 5. On this account the fit of the experimental DTG spectrum in the framework of monoenergetic approximation aiming to extract both parameters would lead to essential errors the larger the width of the energetic spectrum $\varphi(E)$.
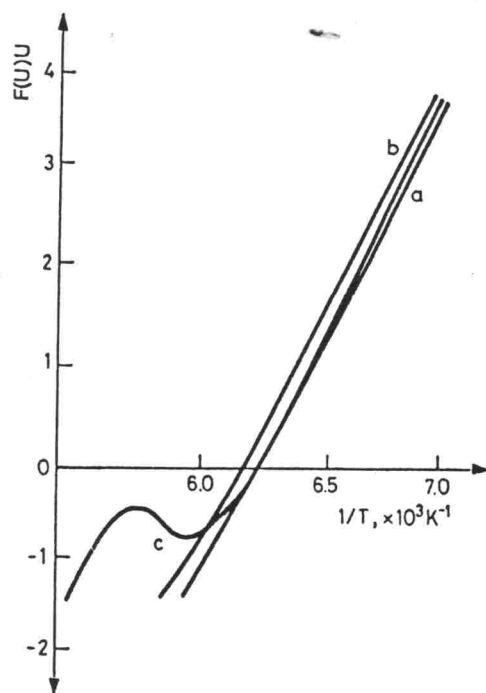

Fig. 6 The linearized plots of the temperature dependences of thermostimulated gas release curve from a sample where two parallel first order reactions occur; the discrete spectra of the activation energies of the reactions are given in Fig. 4

The same DTG curves replotted in the functional scale of the first order kinetics are given in Fig. 6. It is seen that the initial part of heating (from T_0 to T_m) DTG curves satisfactory rectified and the slope (tangent) of the straight line defines the value of E_1. The presence of the high energy component of the activation energy spectrum is found by a cusp on the linearized curve. With the difference growth the slope tangent of the high

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Zusammenfassung — Die Möglichkeiten des Softwarepaketes THERMOKIN zur Auswertung experimenteller Daten von thermischen Feststoffzersetzungen werden beschrieben. Das Softwarepaket ermöglicht die Simulation von Feststoffreaktionen, die Auswertung der Ergebnisse von verschiedenen thermoanalytischen Methoden, wie z.B. TG/DTG, DSC, Analyse der entstehenden Gase usw. Durch das Softwarepaket wurde es ermöglicht, ein adäquates Modell für die Feststoffreaktion auszuwählen und die Reaktionsparameter sowie deren Fehler zu berechnen. Unter Anwendung dieses Softwarepaketes können einerseits die Ergebnisse aus den verschiedensten thermoanalytischen Verfahren interpretiert und andererseits die optimalen Reaktionsbedingungen für die jeweiligen untersuchten Substanzen ermittelt werden.

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