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PROBLEMS OF THE CHARACTERIZATION OF THERMOANALYTICAL PROCESSES BY KINETIC PARAMETERS

Part I

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On the basis of many experiments and theoretical reflections, the authors showed earlier that the courses of non-isothermal analytical curves are strongly influenced by the experimental conditions, and therefore the sense of kinetic parameters calculated from these curves is fictitious and their determination is uncertain.

In the present work some further problems of this question are discussed. It was found that with combinations of strongly differing parameters nearly identical TG curves can be produced, and this situation cannot be improved even by orthogonal polynomial transformation. Further integral methods, using linearization, the estimation of the parameters is poor.

The model transformed according to the conditions of the quasi-isothermal — quasi-isobaric technique leads to contradictions, unambiguously showing the correlation existing between the parameters.

The view that the parameters A, E and n of the Arrhenius relation can reliably be calculated from thermoanalytical curves has now persisted for more than two decades, in spite of the fact that the practical application of the calculation method involves many difficulties. Thermoanalysts have therefore tried to develop various new calculation methods, or to apply corrections to the earlier methods in order to eliminate the obstacles [1–41]. The great number of these researchers itself implies admission of the errors, and has given rise to certain criticism [42–55]. However the struggle has not been given up. As a concession the fiction of "formal" kinetics was born, which attributed to kinetic parameters not a real but some fictitious sense.

Information content of conventional thermoanalytical curves

The contradictions connected with this question can be studied in Fig. 1 and Table 1. Every curve of the Figure represents the decomposition of calcium carbonate. The differences between the courses of the individual curves are due to the various experimental conditions. Especially conspicuous are the differences between the shapes of curves traced under dynamic (curves 1–8) and under quasi-isothermal – quasi-isobaric conditions (curves 9–12).

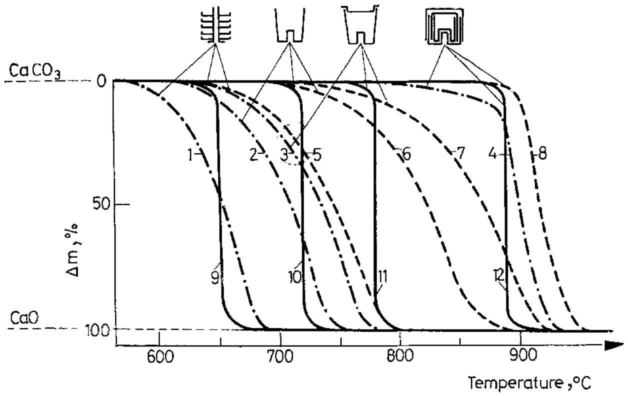


Fig. 1. TG curves of calcium carbonate, traced by using various heating rates, sample amounts and sample holders. Curves 1—4: dynamic heating rate 2.5°/min; 50 mg $CaCO_3$; curves 5—8: dynamic heating rate 10°/min; 250 mg $CaCO_3$; curves 9—12: quasi-isothermal heating, 0.5 mg/min (58); 250 mg $CaCO_3$; curves 1, 5, 9: multiplate sample holder (60); curves 2, 6, 10: uncovered crucible (60); curves 3, 7, 11: covered crucible; curves 4, 8, 12: labyrinth crucible (58)

Table 1 contains the parameters computed from curves 1—8 with four different methods of kinetic calculation. These values show big variations, depending on both the experimental conditions and the calculation methods, despite the fact that each of them represents the very same simple decomposition reaction.

In the knowledge of this contradiction, we earlier [56—58] considered it doubtful that it is possible to draw unambiguous and useful conclusions regarding the kinetics of reactions from the courses of conventional thermoanalytical curves.

We examined the correlations between the shapes of thermoanalytical curves and the mechanisms of the elementary chemical and physical processes (Table 2) occurring. Our investigations convinced us that, under the conditions of dynamic thermoanalytical examinations, the course of the transformation is not defined by the chemical reaction itself taking place on the phase boundary (Table 2, b), but by the elementary physical processes slower by several orders of magnitude, i.e. the experimental conditions which influence these processes. Of these, gas and heat transports play the most important roles (Table 2, c). Accordingly, the courses of the thermoanalytical curves are characteristic rather of the experimental conditions than of the reaction examined.

Experience shows that powdered material of poor thermal conductivity is not able to take up instantaneously from its surroundings the heat necessary for the progress of the transformation. Consequently, the progress of conversion is controlled in most cases by the heat transport, this being the slowest of the processes. The difference in the courses of curves 8 and 12 in Fig. 1 serves as proof of this. Under the experimental conditions of the graph, there was a difference only in the rate of heat absorption amounting to about two orders of magnitude.

Table 1

Kinetic parameters (n, E, A) calculated with different methods on the basis of the curves shown in Fig. 1

Sample holder	TG curve in Fig. 1.	Kissinger	Freemann—Carrol		Horowitz—Metzger		Zsakó		
		n	n	E	n	E	n	E	A
Polyplate	1	0.7	0.0	124	0.5	114	1.0	90	$2 \cdot 10^{14}$
	5	0.5	1.5	71	0.3	78	2.0	68	$2 \cdot 10^{14}$
Pt crucible	2	0.5	1.6	69	0.3	78	1.0	70	$3 \cdot 10^{14}$
	6	0.5	2.0	87	0.2	92	1.0	72	$7 \cdot 10^{13}$
Pt crucible with cover	3	0.5	1.0	80	0.3	77	0.5	54	$2 \cdot 10^{10}$
	7	0.6	0.8	72	0.3	80	0.5	52	$2 \cdot 10^{9}$
Labyrinth crucible	4	1.0	0.0	61	0.7	99	0.0	66	$5 \cdot 10^{18}$
	8	1.0	0.4	209	0.8	162	0.0	106	$2 \cdot 10^{18}$

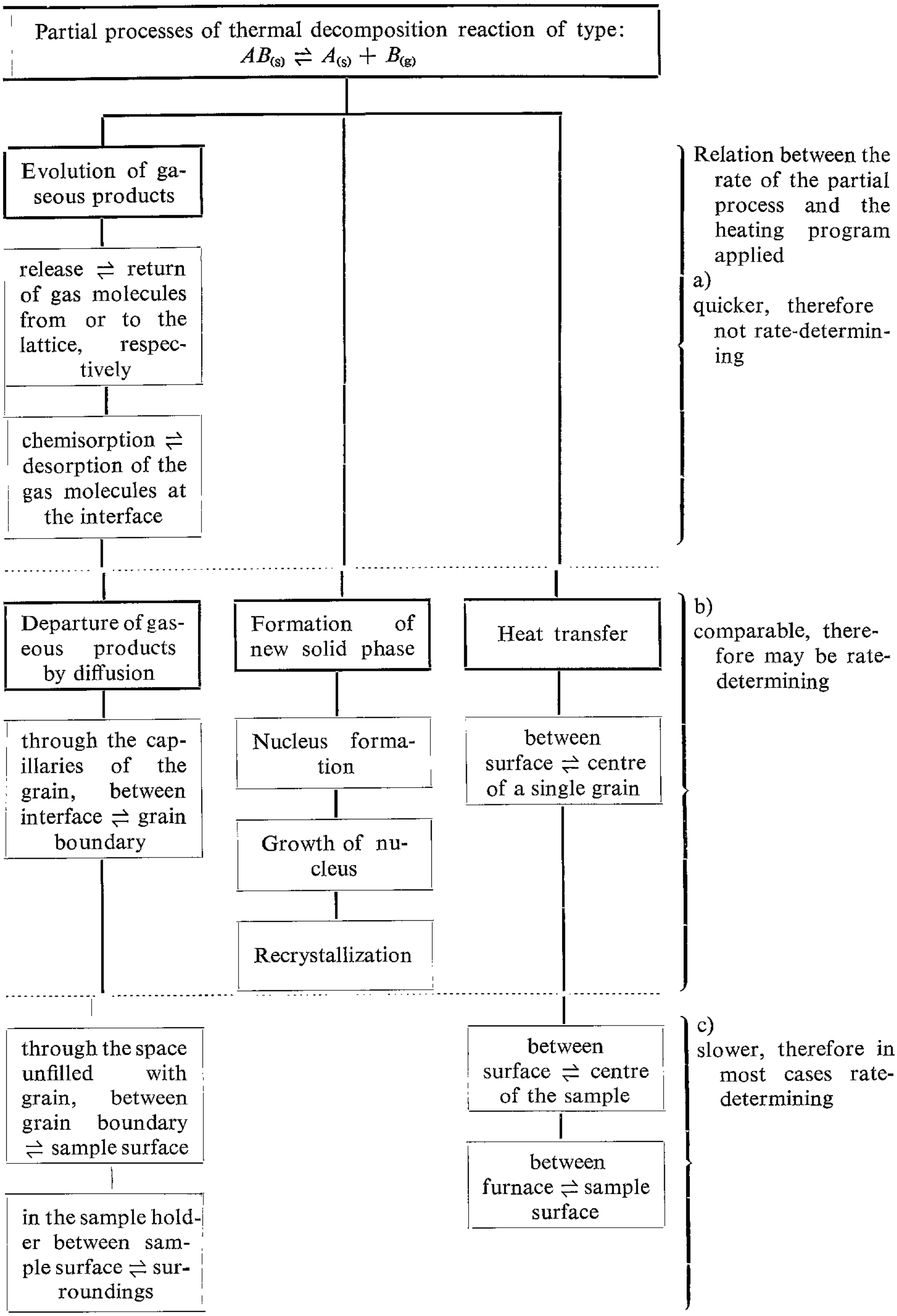
It is also easy to see that in the case of reactions leading to equilibrium the progress of the dissociation is fundamentally influenced by the continuous and uncontrollable changes in the concentration of the gaseous decomposition products in contact with the solid material [59], and by the experimental conditions influencing the above changes.

The magnitude of this effect can be judged from the difference in the courses of curves 6 and 8 in Fig. 1. In the case of curve 6 the concentration of the gaseous decomposition products in the vicinity of the sample continuously changed, while it remained constant during the whole time when curve 8 was recorded.

The course of the transformation can be further modified among others by nucleus formation and nucleus growth, as well as by recrystallization processes

Table 2

Elementary chemical and physical processes playing a part in thermal decomposition reactions leading to equilibrium



influencing the porosity of the new phase and the diffusion rate of the gaseous decomposition products (Table 2).

For the sake of completeness it is to be noted that the mechanism of the partial processes cannot actually be surveyed at all, because with the progress of the conversion the phase boundary continuously migrates from the direction of the grain surface towards the centre and as a consequence the conditions of mass and heat transport continuously change.

Information content of quasi-isothermal–quasi-isobaric TG curves (Q–TG)

The question arises as to what kind of information regarding the kinetics of the reactions may be obtained from Q–TG curves traced with the quasi-isotnermal–quasi-isobaric technique [56–58].

The point of the quasi-isothermal heating technique lies in the condition that the heating regulator system establishes a difference between the furnace and sample temperatures such that the transformation should take place at a very low and strictly constant rate, selected in advance. It is experienced in such cases that no temperature drop occurs within the sample, and there is sufficient time for the uptake of the heat amount necessary for the conversion.

Due to the constant decomposition rate, the partial pressure of the gaseous decomposition products in contact with the solid phase (Fig. 1, curves 9–12) also remains constant (quasi-isobaric). This is especially valid when the labyrinth sample holder is used, in which a "self-generated" atmosphere is formed immediately at the beginning of the transformation and the 1 atm partial pressure of the gaseous decomposition products stays constant until the end of the conversion (curve 12).

The temperature of the sample becomes spontaneously adjusted to the value at which the rate of the transformation may remain constant. In the case of reactions leading to equilibrium, this temperature corresponds to the instantaneous state of equilibrium defined by the concentration of the gaseous decomposition products too (Fig. 1, curves 1–12).

In reactions not leading to equilibrium (Fig. 2, curve b), the temperature of the sample is established independently of the concentration of the gaseous decomposition products.

The Q–TG curve, recorded as a function of this temperature, changing in a special way, yields other information regarding the kinetics of the transformation than does the conventional TG curve. Two basic types of Q–TG curves can be distinguished.

The conversion takes place according to zero order if the course of the Q–TG curve is similar to that of curve *a* in Fig. 2. In such cases the progress of the transformation is governed by the heat transport, this being the slowest process. The chemical reaction occurring at the phase boundary (Table 1, *a*) is too rapid to be able to exert any influence upon the course of the transformation. It has been found

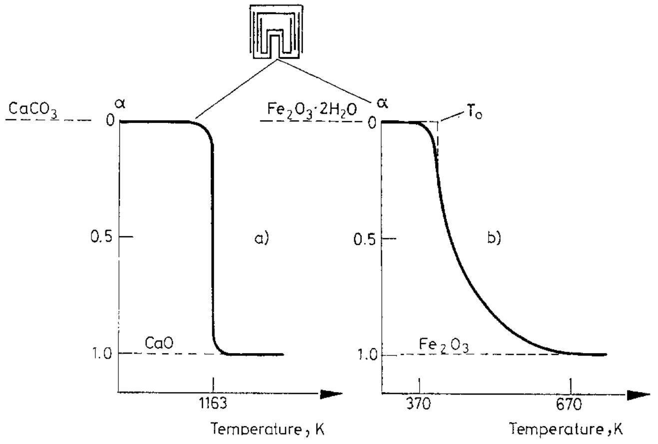


Fig. 2. Two basic types of thermogravimetric curves traced under quasi-isothermal and quasi-isobaric conditions (Q–TG); a) zero-order transformation, b) not zero-order transformation

that the simple dissociation reactions of inorganic compounds leading to equilibrium occur in this way.

Curve *b* in Fig. 2 illustrates transformations which do not take place according to zero order, and in which the chemical reaction itself is often the slowest process, defining the course of the conversion. This kind of Q–TG curve may be obtained in reactions of inorganic and organic compounds not leading to equilibrium, or if consecutive and overlapping reactions are taking place, or if the reaction becomes diffusion-controlled due to the formation of a compact new phase which is hard to cross for the gaseous decomposition products.

Preliminary conclusion

In accordance with the above, kinetic calculations, performed on the basis of thermoanalytical curves traced under dynamic heating conditions, yielded very little information concerning the kinetics of the reactions examined.

Therefore, in our opinion the Arrhenius equation, being taken from homogeneous kinetics, cannot be applied to non-isothermal heterogeneous reactions, since the conditions of the Arrhenius equation are not fulfilled under the circumstances of these latter ones. In these cases the model of transport theory must be taken into consideration.

It was also demonstrated how much the courses of the curves are influenced by the experimental conditions. Therefore, even in the case of the strictest standardization of the experimental conditions, the curves obtained in parallel examinations would run in a domain of varying width.

The reliability of kinetic calculations becomes even more questionable if we raise the question of one-to-one correspondence between the ternary parameter system (A, E, n) and the TG curve. We decided, therefore, to perform a critical study of the mathematical bases of the kinetic calculations. We wish to report on the results of our examinations in the present and subsequent papers.

The TG curve as solution curve of the Arrhenius differential equation

We selected as the subject of our research those reaction kinetic calculations which are based on the data of TG curves. We did this because, of all the thermal effects, the weight changes of the sample demonstrate most truly the progress of the conversion, and there exists a strict numerical correlation between weight changes and progress not as in the case of DTA or DSC measurements.

For the determination of kinetic parameters of reactions involving weight changes, the TG curve can be studied on the basis of the following considerations:

$$\frac{\mathrm{d}\,\alpha(t)}{\mathrm{d}t} = k \cdot f(\alpha(t)) \tag{1}$$

where α is the reaction coordinate, k the constant of reaction rate, and t the time.

In reactions with weight changes the reaction coordinate is the weight fraction of the converted material:

$$\alpha = \frac{m_0 - m}{m_0 - m_v} \tag{2}$$

where m_0 is the initial, m the actual, and m_v the final amount of the material. Accordingly,

$$0 \leq \alpha(t) \leq 1$$

$$\text{and } \alpha(0) = 0 \qquad\qquad \text{and } \alpha(t_v) = 1$$

where t_v is the time when the process is completed. The usual form of function $f(\alpha(t))$ is

$$f(\alpha(t)) = (1 - \alpha(t))^n \tag{3}$$

where n is the reaction order.

It is to be noted that many relationships are known for the type of the function $f(\alpha)$, depending on the rate-determining thermal process. We performed our examinations with form (3).

According to Arrhenius, the reaction rate is defined by the absolute temperature (T) and the activation energy (E):

$$k(T) = A \cdot e^{-\frac{E}{RT}} \tag{4}$$

where A is the pre-exponential factor, R the universal gas constant and E the activation energy.

With the application of Eqs (1), (3) and (4) we obtain the following differential equation

$$\frac{\mathrm{d}\,\alpha(t)}{\mathrm{d}t} = A \cdot \exp\left(-E/RT(t)\right) \cdot \left(1 - \alpha(t)\right)^{n} \tag{5}$$

Defining the linear heating program,

$$T = T_0 + \frac{\mathrm{d}T}{\mathrm{d}t} \cdot t = T_0 + G \cdot t \tag{6}$$

where T_0 is the initial temperature (K) and G the heating rate (°/min), we obtain

$$\frac{\mathrm{d}\,\alpha(T)}{\mathrm{d}T} = \frac{A}{G} \cdot \exp(-E/RT) \cdot \left(1 - \alpha(T)\right)^{n*} \tag{7}$$

This separable differential equation can be integrated after separation of the variables.

The aim of mathematical examinations

We can by no means be satisfied with the fact that many arguments have clearly shown that relation (5) generally cannot be regarded as the real physicochemical model of the process examined (Fig. 1, Table 1).

In order to be able to clarify the problem one has to make investigations in two important directions. On the one hand, it is necessary, on the basis of thorough thermodynamic and operational examinations of thermal processes, to try to establish a theoretical model containing the physical and chemical transport processes together. However this task still requires much research work.

On the other hand, it seems necessary to find out the actual reliability of application of the widely-used relation (5), generally regarded only as an apparent model, to thermoanalytical problems. This is in fact the aim of our work.

For the determination of the validity of Eq. (5), regarded as an empirical model, we carried out examinations in several directions.

First, we performed mathematical examinations in order to find out whether, by any appropriate transformation of the TG curve, we could obtain features which are in univocal connection with the apparent kinetic parameters, their application at the same time serving for the better estimation of the parameters. Figure 3 demonstrates the routes of these calculations. While part "*a*" of the Figure illustrates the conventional method of determining the parameters, part "*b*" shows the way of searching for transformation in order to find features for the better estimation of the apparent kinetic parameters.

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* Here the fundamental problem of relation (7) should be emphasized, *viz.* that the equation is valid only if the temperature of the sample increases in a strictly linear way. It is however well-known that this condition can never totally be fulfilled under dynamic heating conditions.

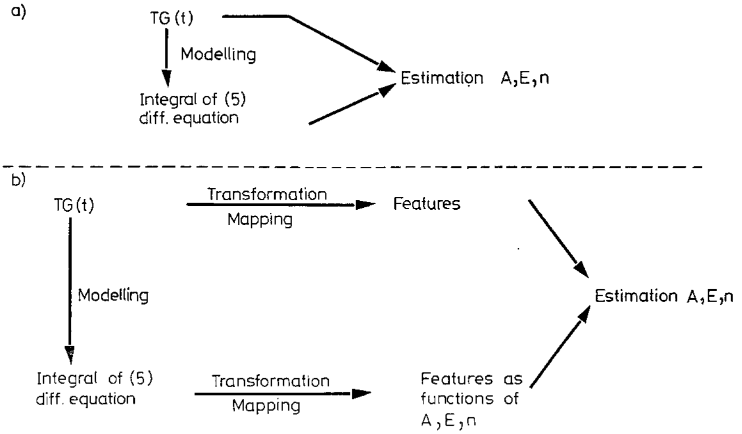

Fig. 3. Conventional (a) and present (b) method of estimation of kinetic parameters

As regards the transformations, in our present paper we wish to report on the application of orthogonal polynomials, while the results of the application of moments, the Karhunen–Loeve transformation and other mappings will be described in the following parts of the series.

We performed further mathematical examinations with regard to the reliability of the estimation of the apparent kinetic parameters, in order to establish the applicability of model (5) to thermoanalytical measurements.

In connection with this field, in our present paper we deal with the examination of the widely-used technique of estimation with the integrated method of the linearized form of the model. In the following papers of the series the problems of variable transformations and non-linear estimation will be discussed.

We think that, as regards the applicability of the model, a very important task is to examine the model under special experimental conditions. Therefore, we studied the question of what conclusions can be drawn from the application of the model under the conditions of quasi-isothermal–quasi-isobaric measurements. This problem will also be discussed in detail within the framework of this series.

Application of transformations: orthogonal polynomials

It is a well-known fact that the combinations of various and different parameters yield nearly the same TG curve [21]. These simulation experiments mean that model (5) or (7) is not sensitive to changes in certain parameters. For demonstration of the connection existing between the shape of the curve and the changes in the model parameters, we constructed a series of TG curves with the help of model (7), i.e. with its parameters, which changed between the limits of physical reality (Fig. 4). The data concerning the simulation of the curve series are given in Appendix I.

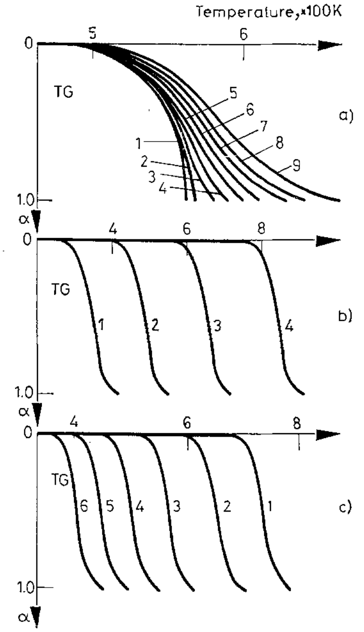

Fig. 4. Influence of changes in the n, E and A parameter values on the courses of TG curves: a) $n = 0.1$, 0.3, 0.6, 0.,9 1.2, 1.5, 1.8, 2.1 and 2.4 in the sequence of curves 1–9, $E = 40$, $A = 10^{14}$; b) $E = 25$, 35, 45 and 55 in the sequence of curves 1–4, $n = 1.05$, $A = 10^{14}$; c) $A = 10^{10}$, 10^{12}, 10^{14}, 10^{16}, 10^{18} and 10^{20} in the sequence of curves 1–6, $E = 40$, $n = 1.05$.

The simulation examinations clearly demonstrate the well-known compensation effect, i.e. the correlation between the parameters A and E.

We tried to find out whether, in the application of orthogonal polynomials, their coefficients are sensitive to changes in the parameters or not. If there are polynomial coefficients sensitive to changes in the parameters, then from the coefficients determined on the basis of the real TG curve one can draw conclusions regarding the parameters.

For the clarification of this problem we proved first that a TG curve described by a finite number of discrete values can be constructed with given accuracy with an orthogonal polynomial of m-th degree, i.e. there is a one-to-one correspondence between the TG curve and the coefficients of orthogonal polynomials of m-th degree. Appendix II contains these proofs.

In accordance with the description in Appendix III we produced an orthogonal polynomial system and fitted it to the numerically simulated TG curves as described in Appendix IV. We depicted graphically the changes in the first six coefficients as functions of the individual kinetic parameters (Figs 5–7).

These examinations showed that the changes of the pre-exponential factor (A) in the domain examined were not reflected in the changes of the coefficients of the polynomial systems. With variation of the activation energy (E), little effect can be observed only in the 24 – 35 kcal/mole domain. Only the reaction order has an effect which can be detected univocally.

For the thermoanalytical interpretation of the above results let us use the well-known concept: Two TG curves (TG_1 and TG_2) are different if the $(A_1, E_1, n_1) \neq \neq (A_2, E_2, n_2)$ inequality is valid. Two curves are identical if their reaction kinetic parameters are equal.

The basis of reaction kinetic calculations is the conviction that only one parameter triplet belongs to a given TG curve, and only one curve belongs to a given triplet of parameters.

In the course of calculations it turned out that, though theoretically there exists a one-to-one correspondence between a given simulated TG curve and the coefficients of its approximating orthogonal polynomial system, and consequently various

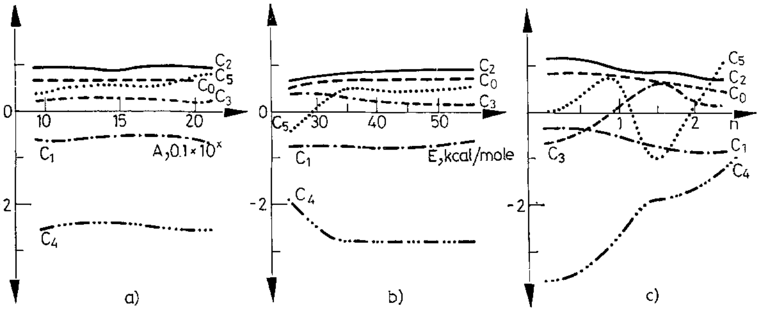

Fig. 5. Variation of the coefficients of the Legendre polynomials: a) with the pre-exponential factor; b) with the activation energy; c) with the reaction order

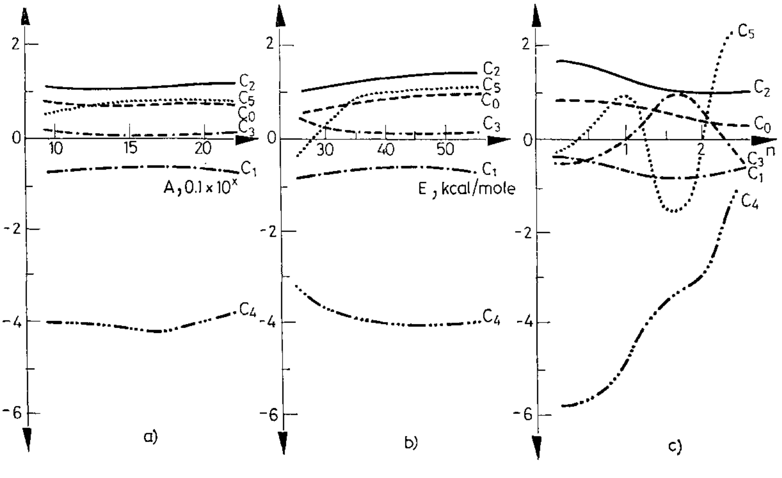

Fig. 6. Variation of the coefficients of the Tchebichef polynomials: a) with the pre-exponential factor; b) with the activation energy; c) with the reaction order

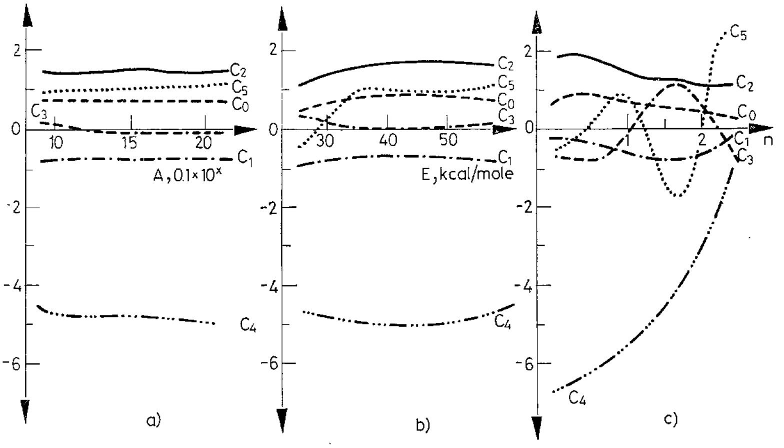

Fig. 7. Variation of the coefficients of the Gegenbauer polynomials: a) with the pre-exponential factor; b) with the activation energy; c) with the reaction order

coefficients belong to various TG curves, several different TG curves do not belong to the same coefficients.

The coefficients of the orthogonal polynomial system approximating the various TG curves, made by changing the pre-exponential factor and the activation energy, are insensitive towards these changes. This means that TG curves represented by orthogonal polynomials are not of different shapes, i.e. they do not correspond to the different E and A parameters.

Hence, this transformation does not yield features which would improve the estimation of kinetic parameters. Furthermore, the results of this examination seem to support indirectly the fact that the increase of E shifts the TG curve solely in the direction of increasing temperature, and the increase of A only in the direction of decreasing temperature ranges (Fig. 4). Hence, in the knowledge of the temperature interval of the TG curve, only some kind of product-like connection between A and E can be obtained. Accordingly, from a TG curve traced under the conditions of a single dynamic heating program the estimation of A and E is poor and so the estimated parameter values can hardly be used by the thermoanalyst for characterization of processes and materials.

The reliability of parameter estimation

We also examined the reliability of the estimation of reaction kinetic parameters for the case when the parameters are estimated by the least squares method using integrating method of the linearized form of model (7).

The reliability of the parameter estimation may be characterized by examination of the coefficient matrix of the linear equation system of three unknowns, obtained by partial derivation according to the least squares method. Let us write again the equation

$$\frac{\mathrm{d}\,\alpha(T)}{\mathrm{d}T} = A^* \cdot \exp(-E/RT)(1-\alpha(T))^n \tag{8}$$

where

$$A^* = \frac{A}{G}$$

the logarithmic form of which is

$$\ln\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \ln A^* - E/RT + n \cdot \ln(1-\alpha). \tag{9}$$

By using this for the related values $\left(T_i, \alpha_i, \frac{\mathrm{d}\alpha_i}{\mathrm{d}T_i}\right)$ measured, we estimate values E, $\ln A^*$ and n with the method of least squares:

$$F = \sum_{i=1}^{N}\left[\ln\frac{\mathrm{d}\alpha_i}{\mathrm{d}T_i} - \ln A^* + E/RT_i - n \cdot \ln(1-\alpha_i)\right]^2. \tag{10}$$

By making the partial derivatives zero, let us find the minimum of the above function:

$$\frac{\partial F}{\partial \ln A^*} = 0; \quad \frac{\partial F}{\partial E} = 0; \quad \frac{\partial F}{\partial n} = 0.$$

This means:

$$\begin{aligned}
&-\sum_{i=1}^{N}\left[\ln\frac{\mathrm{d}\alpha_i}{\mathrm{d}T_i} - \ln A^* + E/RT_i - n \cdot \ln(1-\alpha_i)\right] = 0\\
&\sum_{i=1}^{N}\left[\ln\frac{\mathrm{d}\alpha_i}{\mathrm{d}T_i} - \ln A^* + E/RT_i - n \cdot \ln(1-\alpha_i)\right] \cdot \frac{1}{RT_i} = 0\\
&-\sum_{i=1}^{N}\left[\ln\frac{\mathrm{d}\alpha_i}{\mathrm{d}T_i} - \ln A^* + E/RT_i - n \cdot \ln(1-\alpha_i)\right]\ln(1-\alpha_i) = 0.
\end{aligned} \tag{11}$$

Let us introduce the following symbols and rearrange the equation:

$$\begin{aligned}
&\ln A^* = B; && \sum_i \ln(1-\alpha_i) = b; && \sum_i \frac{1}{(RT_i)^2} = f;\\
&\sum_i \ln\frac{\mathrm{d}\alpha_i}{\mathrm{d}T_i} = c; && \sum_i \frac{1}{RT_i}\ln(1-\alpha_i) = \mathrm{d}; && \sum_i \frac{1}{RT_i} \cdot \ln\frac{\mathrm{d}\alpha_i}{\mathrm{d}T_i} = g;\\
&\sum_i \frac{1}{RT_i} = a; && \sum_i \ln^2(1-\alpha_i) = e; && \sum_i \ln(1-\alpha_i) \cdot \ln\frac{\mathrm{d}\alpha_i}{\mathrm{d}T_i} = h.
\end{aligned} \tag{12}$$

This assumes the following matrix form:

$$\begin{bmatrix} N & -a & b \\ -a & f & -d \\ b & -d & e \end{bmatrix} \cdot \begin{bmatrix} B \\ E \\ n \end{bmatrix} = \begin{bmatrix} c \\ -g \\ h \end{bmatrix} \tag{13}$$

The problem given above is:

$$\mathbf{A} \cdot \mathbf{x} = \mathbf{y}$$

where $\mathbf{A}$ is the coefficient matrix, $\mathbf{x}$ the vector of the parameters $[\mathbf{x}^{\mathrm{T}} = (B, E, n)]$ to be determined, and $\mathbf{y}$ the vector $[\mathbf{y}^{\mathrm{T}} = (c, -g, h)]$ obtained from the measured values.

We obtain the accuracy of the solution of the equation system from the following expression:

$$\frac{\|\Delta\mathbf{x}\|}{\|\mathbf{x}\|} = \|\mathbf{A}\| \cdot \|\mathbf{A}^{-1}\| \cdot \frac{\|\Delta\mathbf{y}\|}{\|\mathbf{y}\|} \tag{14}$$

The product $\|\mathbf{A}\| \cdot \|\mathbf{A}^{-1}\|$ may give information regarding the measure of the relative uncertainty of the solution. This product is called the condition number (cond(A)) of the equation system. If it is large then the solution is unreliable. For example, if cond(A) is of the order of magnitude of 10^5, then we have to know vector $\mathbf{y}$, consisting of the values measured, with an accuracy of 0.0001 % to be able to obtain a 10 % accuracy of the solution.

With the application of the related values $\left(T_i, \alpha_i, \frac{d\alpha_i}{dT_i}\right)$ of the TG curves computed earlier by simulation, we took the above linear equation system, determined the solution and examined the condition number of the coefficient matrix.

The values obtained show that the condition number of the linear equation system lies between $3 \cdot 10^4$ and $3.5 \cdot 10^5$, demonstrating that the estimation of the parameter values is rather poor. As a conclusion, we may state that on the basis of a single TG curve traced under dynamic heating conditions the reaction kinetic parameters cannot be properly estimated and univocally calculated.

Estimation of kinetic parameters in the case of the quasi-isothermal–quasi-isobaric measuring technique

a) *Processes taking place at constant temperature*

In the knowledge of the above discussion, let us consider the TG curve of $CaCO_3$ recorded by the quasi-isothermal–quasi-isobaric measuring technique (Fig. 3a). It can be seen that after the process has started the system sets into a constant temperature and maintains this until the decomposition is completed.

Let us apply the following wide-spread equation for this case, too:

$$\frac{\mathrm{d}\,\alpha(t)}{\mathrm{d}t} = A \cdot \exp\left(-E/RT(t)\right)\left(1-\alpha(t)\right)^{\mathrm{n}}. \tag{15}$$

Since the quasi-isothermal–quasi-isobaric measuring technique ensures a constant decomposition rate, it can be assumed that during the full time period of the decomposition the following is valid:

$$\frac{\mathrm{d}\,\alpha(t)}{\mathrm{d}t} = C \text{ (constant)}$$

As the thermal curve shows, the T value is also constant in the course of the decomposition ($T = T_0$). Accordingly, Eq. (15) changes as follows:

$$C = A \cdot \exp\left(-E/RT_0\right)\left(1 - \alpha(t)\right)^{\mathrm{n}} \tag{16}$$

As $\alpha(t)$ varies between 0 and 1, the above product can only be constant if each member of it is constant, since the parameters E and A are supposed not to vary in the course of one decomposition process. However, this is possible only if $(1-\alpha)^{\mathrm{n}} \equiv 1$, and this identity can be valid only if $n = 0$, which means that the order of the kinetics is equal to 0, without physical meaning. If physical-chemical meaning can be attributed to the above model, the physical process (mass transport, heat transport) is covered by the chemical one, which is orders of magnitude more rapid.

In such cases it is senseless to speak about the interpretation of the reaction kinetic parameters, since these parameters can be characteristic only of the physical conditions of the process. A further counter argument against the application of the Arrhenius equation to this case is that under quasi isothermal circumstances the boundary conditions, set up originally by Arrhenius, are not fulfilled.

Let us examine the problem further. As $(1-\alpha)^{\mathrm{n}} \equiv 1$, it is true that

$$C = A \cdot \exp\left(-E/RT_0\right)$$

or (17)

$$C = e^{\ln A - E/RT_0}.$$

From this one can unambiguously conclude that

$$\ln A - E/RT_0 = \text{constant}.$$

On the above basis it can be stated that, in the case of zero-order processes, from a single curve recorded by the quasi-isothermal–quasi-isobaric measuring technique, the values of A and E themselves can not be determined, but only their relationship.

b) *Processes taking place at varying temperatures*

Let us examine the question further in the case of processes taking place at varying temperatures, recorded by the quasi-isothermal–quasi-isobaric measuring technique. See curve of $Fe(OH)_3$ (Fig. 2b).

In this case there are theoretical obstacles to the correct application of the Arrhenius equation.

In the case of the linear heating program discussed earlier it can rightly be written:

$$\frac{d\,\alpha(T)}{dT} = \frac{A}{G} \cdot \exp(-E/RT)(1 - \alpha(T))^n \tag{18}$$

since α is unambiguously dependent upon the temperature, which is a linear function of time. Therefore, the rate law can be described as a function of the temperature.

When recordings made by the quasi-isothermal–quasi-isobaric measuring technique are used, if the process takes place at only one temperature point (T_0), Fig. 2a can be regarded as involving a function only of time, and thus:

$$\frac{d\,\alpha(t)}{dt} = A \cdot \exp(-E/RT_0)(1 - \alpha(t))^n \tag{19}$$

where

$$\frac{d\,\alpha(t)}{dt} = \text{constant.}$$

However, when the temperature of the sample varies in time in the course of measurement by the quasi-isothermal – quasi-isobaric technique, the Q–TG curve resulting from the measurement shows that α is a linear function of time and an unknown function of temperature. Accordingly, $\alpha = \alpha(t, T(t))$ and in this case one must not consider correctly α as a function only of the time or only of the temperature. This is why the Arrhenius equation can not be interpreted in any of the simple forms presented previously. Hence, when processes examined by the quasi-isothermal–quasi-isobaric measuring technique are taking place at varying temperatures, the Arrhenius equation must not be applied, at all, not even as a formal model and consequently no reaction kinetic calculations may be performed with this equation.

*

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Appendix I

Simulation of TG curves

The Arrhenius equation, which forms the basis of the kinetic calculations, can be integrated by separating the variables:

$$\int_{w}^{1} \frac{\mathrm{d}w}{w^{n}} = \frac{1-w^{1-n}}{1-n} = \frac{A \cdot E}{G \cdot R}\left(\frac{e^{-x}}{x} - \int_{x}^{\infty} \frac{e^{-u}}{u}\,\mathrm{d}u\right) = \frac{A \cdot E}{G \cdot R} \cdot p(x)$$

where $w = (1 - \alpha)$

$$x = \frac{E}{RT}.$$

Several methods are known for the determination of $p(x)$. An approximate formula developed by Schlömlich (cited by Doyle [61]) has been applied here:

$$p(x) \simeq (x + 2)^{-1} \cdot x^{-1} \cdot e^{-x} \; \textit{if} \; 10 \leq x \leq 80.$$

By simulation of the series of TG curves the single parameters were varied in the following intervals:

$n \in [0.1; 2.4]$	subject to $E = 40.0, A = 10^{14}$
$A \in [10^{10}; 10^{20}]$	subject to $E = 40.0, n = 1.05$
$E \in [25; 55]$	subject to $A = 10^{14}, n = 1.05$

Thus, the obtained series of curves (Fig. 4) successively show the effects of varying the apparent reaction order, the pre-exponential factor and the activation energy upon the slope of the curve.

Appendix II

Correspondence between the TG curve and the coefficients of orthogonal polynomials

The TG curves are given by values of their functions at equidistant points, i.e. by values α_i ($i = 1, 2, \ldots N$). Thus, each TG curve is transformed to a point of the N-dimensional Euclidean vector space (pre-Hilbert space). Let us fit all TG curves by an orthogonal polynomial of m-th degree, given also by its values at N equidistant points. (Simulation of polynomials is to be seen in Appendix III.) Accordingly, the polynomial, too, can be interpreted as a point of the N-dimensional pre-Hilbert space.

If the fitted polynomial is in the near neighbourhood of the given TG curve, then the fitting is good, and the coefficients of the fitting polynomial unambiguously determine the TG curve. This statement is a consequence of the following theorems.

Let us consider the above X pre-Hilbert space, which is known as linear and normalized. Let be $f \in X$, where f is the representation of some TG curves in pre-Hilbert space. Let us regard all linear combinations $\sum\limits_{i=0}^{m} c_i g_i$ with elements $g_0 \ldots g_m \in X$ and coefficients $c_0 \ldots c_m$, where $\forall\, g_i$ is a linearly independent element of X. $\left(\sum\limits_{i=0}^{m} c_i^0 g_i \text{ is the transformation of some orthogonal polynomial.}\right)$ Let us find the $\sum\limits_{i=0}^{m} c_i^0 g_i$ element for which:

$$\left\| f - \sum_{i=0}^{m} c_i^0 g_i \right\| = \varepsilon = \inf_{c_0 \ldots c_m} \left\| f - \sum_{i=0}^{m} c_i g_i \right\| .$$

If there exists such an element, it is called the *best approximate element.*

Theorem. There exists a best approximate element.

Theorem. If space X is normalized, then only one single best approximate element exists.

Theorem. The pre-Hilbert space is strictly normalized.

Relying on the above theorems, the following can be stated. The linear combination consisting of elements $g_0 \ldots g_m$ best approximating the measured point f has been found. From among these, for the best approximate element it is true that:

$$\left(f - \sum_{i=0}^{m} c_i g_i | g_k \right) = 0 \quad (k = 0,1 \ldots m).$$

As a best approximate element does exist, the above system of equations does have a solution for $c_0 \ldots c_m$. In contrast, let us suppose that another solution for $b_0 \ldots b_m$ also exists. However, because of the unicity of the best approximate element it is valid that:

$$\sum_{i=0}^{m} c_i g_i = \sum_{i=0}^{m} b_i g_i .$$

At the same time, the fact that $c_j \neq b_j$ (for any j) is in contradiction with the linear independence of elements g_i.

Accordingly, the following can be stated.

When examining the TG curve in abstract space, it can unambiguously be approximated within a given limit of error. Further, the unicity of the best approximate curve, as well as that of the coefficients of the approximating system (which is a linearly independent one) has been understood. Subsequently, if our examinations are performed at fixed points and with a given independent system, it can be established that one and only one TG curve belongs to the coefficient system of the approximating orthogonal polynomials.

Appendix III

Simulation of the approximate independent orthogonal polynomial system

The following three kinds of polynomials have been examined as approximate orthogonal systems:

Tchebichef polynomials
Legendre polynomials
Gegenbauer polynomials

All three kinds of polynomials are, in fact, special cases of Jacobian polynomials and satisfy the following assumptions.

Let us examine the closed interval $[-1, +1]$, and let the function $\rho(x) = (1-x)^{\alpha} \cdot (1 + x)^{\beta}$ be positive almost everywhere in this interval and $\alpha > -1$, $\beta > -1$. The polynomials $P_{\mathrm{m}}^{(\alpha,\beta)}(x)$ satisfying these conditions fulfil the following condition of orthogonality, too:

$$\left(P_{\mathrm{j}}^{(\alpha,\beta)}(x) \mid P_{\mathrm{l}}^{(\alpha,\beta)}(x)\right) = K_{\mathrm{l}}\delta_{\mathrm{jl}}$$

where δ_{jl} is the Kroenecker delta, for which

$$\delta_{\mathrm{jl}} = \begin{cases} 1 \text{ if } j = l \\ 0 \text{ in other cases}. \end{cases}$$

The Jacobian polynomials can be produced in explicit form either by the Rodrigues formula or by the recursive method.

If $\alpha = \beta = \frac{1}{2}$ the Tchebichef second-order polynomials are obtained;
$\alpha = \beta = 0$ the Legendre polynomials are obtained;
$\alpha = \beta = 1$ the Gegenbauer polynomials are obtained.

In the fitting algorithm the appropriate kind of orthogonal polynomial has been produced by a general method described by Forsyte [62]. According to this, $\{\phi_{\mathrm{j}}(x)\}_{j=0}^{m}$ can be regarded as an orthogonal polynomial series with arbitrary weight $\rho(x)$, which fulfils the following condition of orthogonality:

$$\sum_{i=1}^{N} \phi_{\mathrm{j}}(x_{\mathrm{i}})\, \phi_{\mathrm{l}}(x_{\mathrm{i}})\, \rho(x_{\mathrm{i}}) = \delta_{\mathrm{jl}}K_{\mathrm{l}}$$

where K_{l} is constant.

By total induction it can be proved that the orthogonal polynomial series constructed in this way complies with the next recursive relation:

$$\phi_{\mathrm{j+1}}(x) = (x - \alpha_{\mathrm{j+1}})\, \phi_{\mathrm{j}}(x) - \beta_{\mathrm{j}}\phi_{\mathrm{j-1}}(x)$$
$$\phi_0(x) \equiv 1;\ \phi_{-1}(x) \equiv 0$$

where $\alpha_{\mathrm{j+1}}$ and β_{j} are dependent on the weight function and on the basic points as well.

Appendix IV

Short description of curve fitting

As can be seen in Appendix I, values of the TG curves recorded at points N (f_i, $i = 1, \ldots N$) corresponding to the chosen parameter combinations have been produced.

As described in Appendix III, values ($\phi_j(x_i)$; $i = 1, \ldots N, j = 0, \ldots m$) of the single elements of the corresponding orthogonal system have similarly been produced.

With values produced in this way the fitting was carried out by the least squares method according to the following formulae.

With the above polynomials the approximation will be:

$$y_m(x) = \sum_{j=0}^{m} c_j\phi_j(x).$$

The weighted sum of squares

$$F(c_0^m \ldots c_m^m) = \sum_{i=1}^{N} \rho(x_i)(f_i - y_m(x_i))^2$$

is minimized by making its partial derivatives with respect to the coefficients zero. Thus,

$$\sum_{j=0}^{m} d_{jl}c_j^m = q_l \, (l = 0, 1 \ldots m)$$

where

$$d_{jl} = \sum_{i=1}^{N} \rho(x_i)\phi_j(x_i)\phi_l(x_i)$$

$$q_l = \sum_{i=1}^{N} \rho(x_i) \cdot f_i \cdot \phi_l(x_i)$$

As the series $\{\phi_j(x)\}$ is orthogonal,

$$d_{jl} = \delta_{jl}K_l .$$

Thus:

$$c_j^m = \frac{q_l}{d_{ll}} .$$

The coefficients c_j obtained in this way are demonstrated as functions of E, A and n in Figs 5–7.

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RÉSUMÉ — A partir de nombreuses expériences et réflexions théoriques, les auteurs avaient démontré auparavant que l'allure des courbes TG non isothermes était fortement influencée par les conditions d'expérience. Pour cette raison, la signification des paramètres cinétiques calculés à partir de ces courbes était fictive et leur détermination incertaine.

Dans le présent travail les auteurs discutent quelques autres problèmes sur cette question. En se servant de combinaisons de paramètres fortement différents on peut produire des courbes TG presque identiques et cette situation ne peut pas être améliorée même par transformation polynomiale orthogonale. En outre, on a trouvé qu'à l'aide de méthodes par intégration et par linéarisation, l'estimation des paramètres est mauvaise.

Le modèle transformé selon les conditions de la technique quasi isotherme — quasi isobare entraîne des contradictions qui indiquent, sans équivoque, les corrélations existant entre les paramètres.

ZUSAMMENFASSUNG — Aufgrund zahlreicher Versuche und theoretischer Erwägungen hatten die Autoren früher gezeigt, daß der Verlauf nicht isothermer analytischer Kurven stark von den Versuchsbedingungen beeinflußt wird und deshalb die Bedeutung der aufgrund dieser Kurven berechneten kinetischen Parameter fiktiv und ihre Bestimmung unsicher ist.

In der gegenwärtigen Arbeit werden einige weitere Probleme dieser Frage erörtert. Die Autoren fanden, daß mit Hilfe von Kombinationen stark verschiedener Parameter nahezu identische TG-Kurven hergestellt werden können und daß dieser Tatsache selbst durch orthogonale Polynomtransformation nicht abgeholfen werden kann. Weiter wurde gefunden, daß mit Hilfe von Integralmethoden unter Anwendung von Linearisierung erhaltene Schätzungen der Parameter ungenau sind.

Das den Bedingungen der quasi-isothermen—quasi-isobaren Technik entsprechend transformierte Modell führt zu Widersprüchen, welche die zwischen den Parametern bestehenden Beziehungen eindeutig zeigen.

Резюме — На основании многих экспериментальных и теоретических размышлений, авторы ранее показали, что ход неизотермических аналитических кривых сильно затрагивается экспериментальными условиями и поэтому смысл кинетических параметров, вычисленных на основе этих кривых, является фиктивным и их определение сомнительно. В настоящем сообщении обсуждены некоторые дальнейшие проблемы этого вопроса. Авторы нашли, что с помощью комбинаций сильно различающихся параметров могут быть получены почти идентичные кривые ТГ и это положение не может быть улучшено даже при ортогональном полиномном превращении. Далее, было найдено, что с помощью интегральных методов и при использовании линейности, вычисление параметров бедное. Модель, преобразованная согласно условий квазиизотермического — квазиизобарного метода приводит к противоречиям, недвусмысленно показывая корреляции, существующие между параметрами.