A CRITICAL REFLECTION UPON THE APPLICATION OF THE ARRHENIUS MODEL TO NON-ISOTHERMAL THERMOGRAVIMETRIC CURVES

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ABSTRACT

The applicability of the Arrhenius model for thermogravimetric curves of non-isothermal heterogeneous thermal reactions was investigated The TG curves have been simulated with selected E, A and n values and their parameter triplets have been estimated by the method of total enumeration It was found that a small change in the simulated curve caused a considerable change in the parameter triplets, i e the parameter estimation problem is ill-conditioned. Examination of the measured TG curves shows that the goodness of estimation continues decreasing because, in this case, the TG curves are deformed by the experimental conditions and by the measurement error. Consequently, the authors deem the Arrhenius model inadequate for the calculation of kinetic parameters from non-isothermal thermogravimetric curves

INTRODUCTION

For about two decades researchers have been trying to develop a calculation method which would be suitable for computing reaction kinetic parameters from thermoanalytical curves on the basis of the Arrhenius model [1]. However, there are many observations which show that this kind of calculation cannot lead to a correct result [2]. So, we pointed out earlier that the course of thermoanalytical curves is characteristic of the experimental conditions rather than of the thermal reaction itself [2–4]. Recently, we also showed that this kind of calculation cannot be performed on the basis of the Arrhenius model because its parameters can be estimated only with very great errors [1,5,6]. The practical significance of the reaction-kinetic interpretation of thermal processes induced us to examine a suitable way of demonstrating numerically the uncertainty of the above-mentioned calculation of kinetic parameters. In our present paper we wish to report on the results of our research.

PARAMETER ESTIMATION OF SIMULATED CURVES WITH TOTAL ENUMERATION

With the help of our examinations, we wanted first to determine how the selection of the examined parameter values and the density of the examined lattice points would influence the goodness of the parameter estimation using total enumeration (see Appendix, Sect. 5).

In order to have at our disposal all the results which were calculated with every one of the possible parameter combinations, we selected total enumeration as an optimization method. The magnitude of the parameters was changed one by one in small steps by computer, to form a three-dimensional fine lattice for the total enumeration.

The work was performed as follows. A simulated curve was prepared with the parameter triplet ($E = 160$ kJ mole^{-1}, $n = 1.1$, $A = 10^{14}$) actually occurring in practice. Thereafter, using the discrete data of this curve, where the number of discrete points was $N = 91$, the extent to which the curves belonging to the lattice points approached the simulated curve was examined.

The examined values of the parameters of the simulated curve were selected in the domain examined with total enumeration in such a way that the value of the parameter triplet of the simulated curve fell in the centre of one of the elementary cells of the parameter value lattice.

The computer changed the value of the parameters by the steps $\Delta E = 0.4$ kJ mole^{-1}, $\Delta n = 0.1$, and $\Delta \log A = 0.125$. As can be seen from these steps, the computer scanned with an appropriate "fineness" the interval in question.

Despite this, as Table 1 proves, the parameters could not be estimated with sufficient accuracy. In Table 1, the parameter values and the average of the squares of the deviations belonging to some examined points of the domain are demonstrated. As can be seen, the "best" average of squares of deviations (point 7) and the second best (point 9) are nearly equal, while the deviation of their parameters is

TABLE 1

Parameters of TG curves fitting the reference TG curve satisfactorily

	n	E	A	Sum of the squares	Temp difference (K)
1	0 6	31 05	$0 237 \times 10^{11}$	0 2996	1 46
2	0 7	34 15	$0 422 \times 10^{12}$	0.1931	0 95
3	0 9	35 95	$0 237 \times 10^{13}$	0 1329	0 65
4	0 9	37 25	$0 749 \times 10^{13}$	0 1270	0 62
5	0 9	38 45	$0 237 \times 10^{14}$	0 1563	0 77
6	1 0	39.75	$0 749 \times 10^{14}$	0 1210	0 59
7	1 0	40 35	$0 133 \times 10^{15}$	0 0714	0 35
8	1 2	40 85	$0 237 \times 10^{15}$	0 1382	0 68
9	1 2	42 15	$0 749 \times 10^{15}$	0 0829	0 41
10	1 2	43.45	$0 237 \times 10^{16}$	0.1184	0 58
11	1.3	45 25	0.133×10^{17}	0.1518	0 74
12	1 4	47 75	$0 133 \times 10^{18}$	0 1991	0 97

significant. It is also worth noting that between the parameters of similarly approaching curves (e.g. curves 4,6 and 10) there are very large differences.

As the data summarized in Table 1 show, no kind of regularity between the parameters which could eventually make easier the search for an optimum, or could serve with directives in this respect can be recognized.

In order to make perceptible the magnitude of the average of squares of deviations, they are converted into temperature difference in the last column. This conversion was performed by stating that the shifting of the two simulated curves by a temperature difference of 1.5 K results in a value of 0.306 for the average of squares of deviations, and so the deviation squares in Kelvin using this ratio are given.

We also examined in what sense the goodness of estimation would change if the magnitude of the lattice used at the total enumeration were reduced to one tenth, i.e. the step intervals to $\Delta E = 0.04$ kJ mole^{-1}, $\Delta n = 0.01$, and $\Delta \log A = 0.0125$.

On the basis of calculations, we could state that although the width of the confidence domain decreased with about one order of magnitude, the length of its axis decreased only to about half, which means that with refinement of the step magnitude the goodness of estimation did not proportionately increase.

In contrast with that described earlier, the situation fundamentally changes if the lattice points of the total enumeration are selected in such a way that the parameter triplet of one of the lattice points of the lattice should be absolutely identical with the parameter values of the simulated curve. In this case, we precisely regained the original parameter triplet or, in other words, the average of squares of deviations of the simulated curve and the best fitting curve became practically zero.

From the above, it follows that if we regard the theoretical Arrhenius curve as the measured TG curve, the real parameters of the calculated TG curve can be estimated by the computer with great probability only with errors, even in the case of very fine step intervals.

THE CONFIDENCE REGION OF PARAMETERS IN THE CASE OF SIMULATED CURVES

Approaching the problems of practical calculations, we also examined the question of what would be the situation if, with a shift of ± 1.5 K we were to mark out an uncertainty band to a simulated curve, what parameter triplets would describe the curves belonging to this band limited by the two envelope curves. We purposely defined the width of this band narrower than the real uncertainty domain of thermogravimetric curves, taking into account that, in practice, we have to account for a greater error.

First, by using six different parameter triplets, we prepared six simulated curves. By means of a computer, we searched, in all the six cases, the minimum and maximum values of the parameters of the sufficiently well-fitting curves, i.e. those situated within the ± 1.5 K uncertainty band.

The results of this calculation are summarized in Table 2. The values of the six

TABLE 2

The minimum and maximum values of TG curve parameters fitting various reference TG curves

	Parameters	Minimum	Simulated values	Maximum
1	A (sec^{-1})	10^6	10^7	10^{12}
	E (kJ mole^{-1})	131	146	223
	n	0	0	0 8
2	A (sec^{-1})	10^6	10^7	10^{12}
	E (kJ mole^{-1})	132	146	224
	n	0 6	1 1	1 8
3	A (sec^{-1})	10^7	10^8	10^{14}
	E (kJ mole^{-1})	226	251	370
	n	0	0	0 4
4	A (sec^{-1})	10^6	10^8	10^{13}
	E (kJ mole^{-1})	203	251	369
	n	0 8	1 1	1 8
5	A (sec^{-1})	10^{12}	10^{14}	10^{18}
	E (kJ mole^{-1})	150	167	209
	n	0	0	0 5
6	A (sec^{-1})	10^{11}	10^{14}	10^{20}
	E (kJ mole^{-1})	136	167	230
	n	0 6	1 1	1 4

parameter triplets, with the help of which the base curves were simulated, are also given. The third and fifth columns of Table 2 contain the minimum and the maximum values of the parameters, respectively.

As the above numerical data also prove, the fluctuations in the values of the parameter triplets are very large despite the narrow (± 1.5 K) uncertainty domain
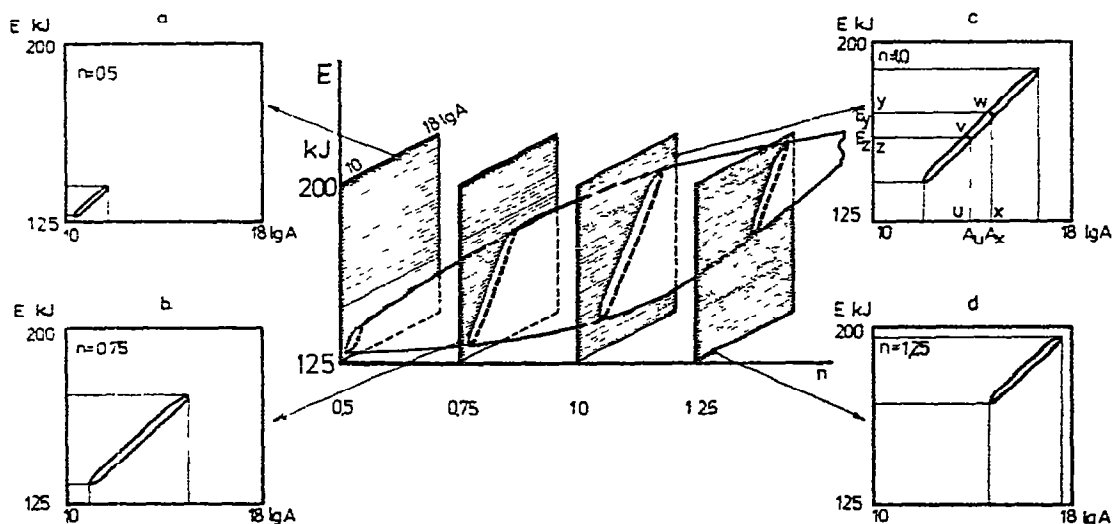

Fig. 1 Confidence region belonging to the parameters of a given basis curve

applied. Thereafter, for curve 6 (in Table 2) simulated with the parameter triplet $E = 167$ kJ mole^{-1}, $n = 1.1$, and $A = 10^{14}$, we collected by means of the computer the parameter triplets of all the curves which fitted better than the two envelope curves shifted by ± 1.5 K. Figure 1 illustrates the stereoscopic picture of the confidence region in the parameter space. Figure 2 illustrates the same confidence region as Fig. 1, but from another aspect (the order of the coordinates was changed).

Every parameter triplet which is an element of this domain should principally be regarded as a "well"-estimated value, since the curves simulated with their help are all situated in the ± 1.5 K uncertainty domain. However, Fig. 2 proves that this deviation in the data of the curve already causes an inadmissible large fluctuation in the estimated values of the parameters. For example, the points $A = 10^{11}$, $E = 130$, $n = 0.5$, and $A = 10^{17}$, $E = 200$, $n = 1.25$ are in this region.

These results supported in every respect our earlier statements, viz. that the application of the Arrhenius model leads to an ill-conditioned parameter estimation problem [1,5,6]. In practice, this means that, even by ensuring the strictest conditions regarding the accuracy of thermoanalytical measurements attainable at present, the fluctuation in the value of the estimated parameter triplet will be very large.

There is an often applied practice with thermoanalysts that, in the course of kinetic calculations, they put restrictions on one of the values of the three parameters, they assume it to be, constant, or take it into constraints, or even totally neglect it. This is carried out by the transformation of the original problem with three variables into a problem with two variables. These modifications and transformations of the original Arrhenius model are not permissible. However, to neither of the three parameters of the Arrhenius model can a superior or an inferior role be attributed since, as can be seen from Figs. 1 and 2, they are all in strong correlation with one another. Consequently, we do not consider the transformation of the Arrhenius model in the above-mentioned sense to be admissible.
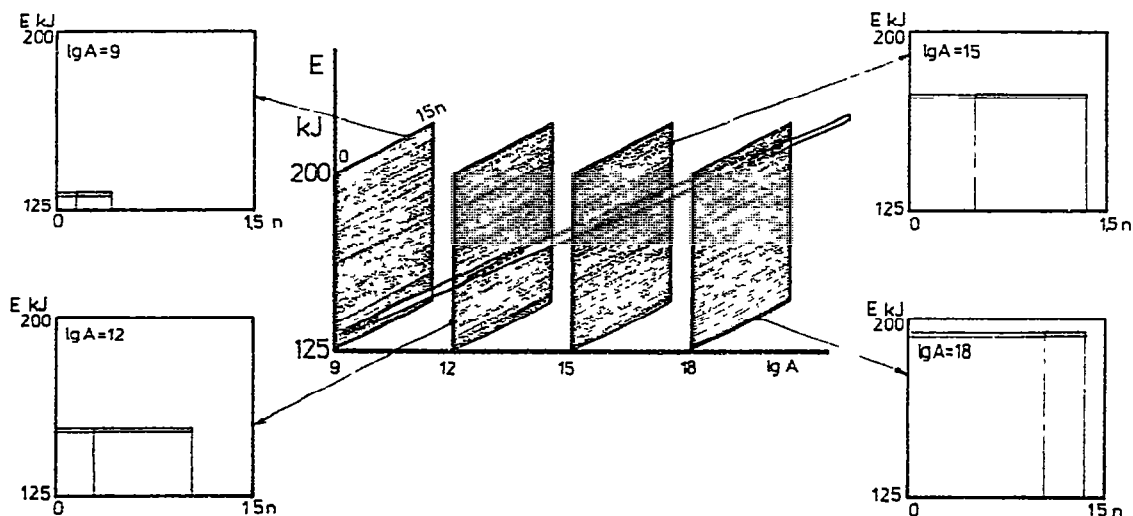

Fig 2 The confidence region demonstrated in Fig 1 from an alternative aspect

Furthermore, even this manipulation cannot lead to accurate results. As an example let us take the case demonstrated by Fig. 1c. Here, for example, we obtained the two-dimensional confidence domain by supposing that the reaction order is $n = 1.05$ and we fixed this. In this case, the supposition corresponded with reality. since at the simulation of the base curve we selected as reaction order $n = 1.05$. From the figure it can be seen that, despite the fixing of the reaction order, the values of the two parameters remained uncertain. From the two-dimensional side pictures of the mentioned figures, it transpires that even if we could accurately determine the value of one of the three parameters and were to use for our calculations a model with two unknowns, by elimination of the third dimension, the uncertainty would decrease but not disappear.

Besides the fixing of the reaction order, let us investigate, on the basis of Fig. 1, in what way the values obtained with various calculation methods would become situated in the confidence region. Let us take two different kinds of calculation method used in practice. According to the two various calculation procedures, the path of estimations is shown by lines u–v–z and x–w–y, respectively, while the resulting parameters are given by the values A_u, E_v and A_x, E_w, respectively. Within the confidence region in question. by means of another calculation method, further pairs of values similarly best approaching the data of the simulated basis curve, can also be found. Accordingly, the estimated values are "fixed" in the confidence domain only by the calculation method applied. It is pointed out, as a reasonable consequence of the above facts. that the estimation can only lose its goodness if the fixed value of the reaction order differs from the real one (e.g. Fig. 1 a,b,d).

THE CONFIDENCE REGION OF PARAMETERS IN THE CASE OF MEASURED TG CURVES

In order to better approach the practice of kinetic calculations, further investigations have been performed with measured TG curves. The courses of the curves have, however, still been regarded as ideal, characteristic solely of the chemical reaction.

On the one hand, the influence of the characteristics of reaction upon the goodness of estimation was examined. Therefore the sublimation and simultaneous dissociation processes of ammonium chloride, the dehydration of calcium hydroxide leading to equilibrium, and the decomposition of anhydrous calcium oxalate leading to non-equilibrium have been chosen as model experiments.

On the other hand, information has also been sought regarding how the changes of physical conditions of measurement influence the goodness of estimation of parameters. This is why sample holders of four different forms were applied to the thermogravimetric examinations, making possible variation of the partial pressure of gaseous decomposition products within wide limits ($p = 1-0.01$ bar) in the vicinity of the sample [7]. So, in common with other researchers who performed kinetic calculations on the basis of conventionally recorded TG curves, as an approximation, we did not consider the influence on experimental conditions of the partial
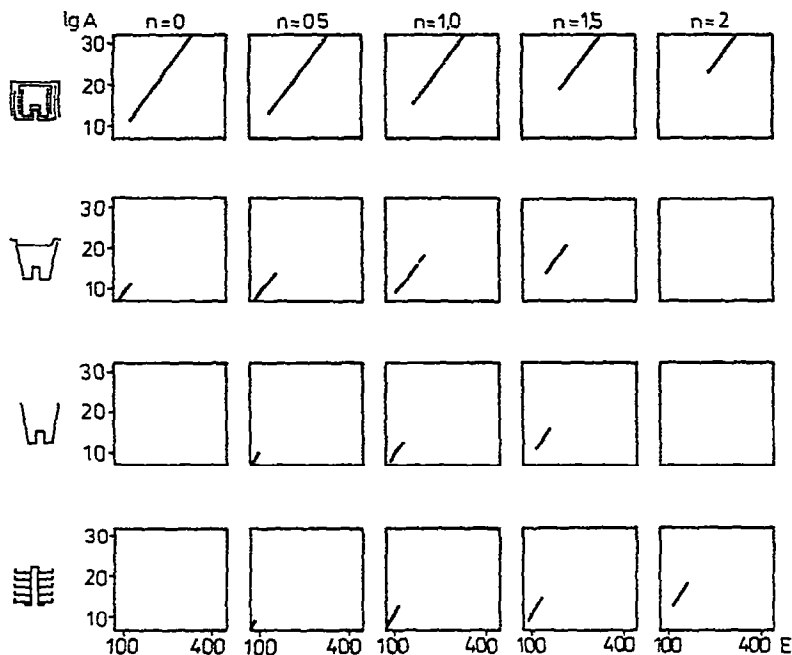
Fig 3 The confidence regions of the TG curve parameters for NH_4Cl

pressure of gaseous products, as well as its effect on the reaction equilibrium.

An uncertainty band of temperature difference ± 2.0 K was marked on the TG curves measured and parameter triplets of curves lying within this domain were sought. Based on the data collected by the computer, Figs. 3–5 have been designed
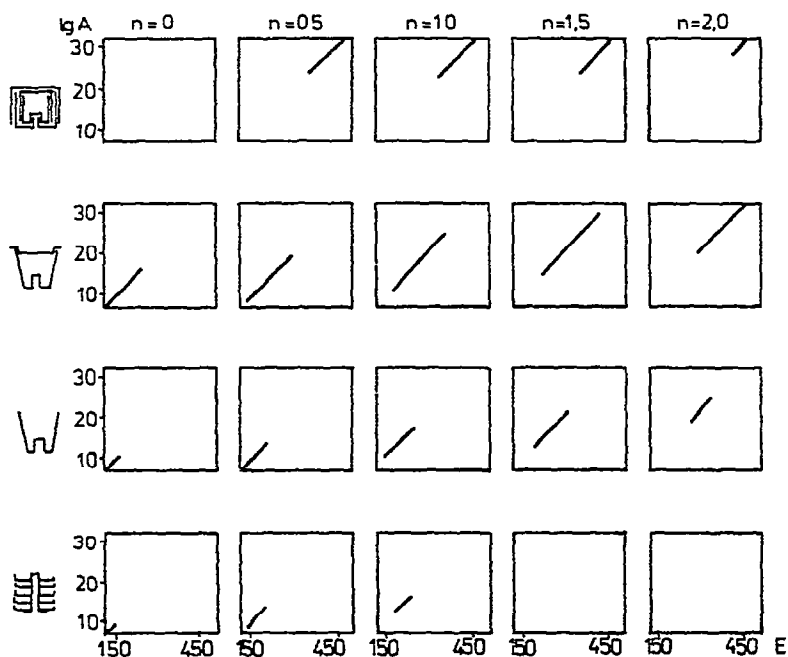

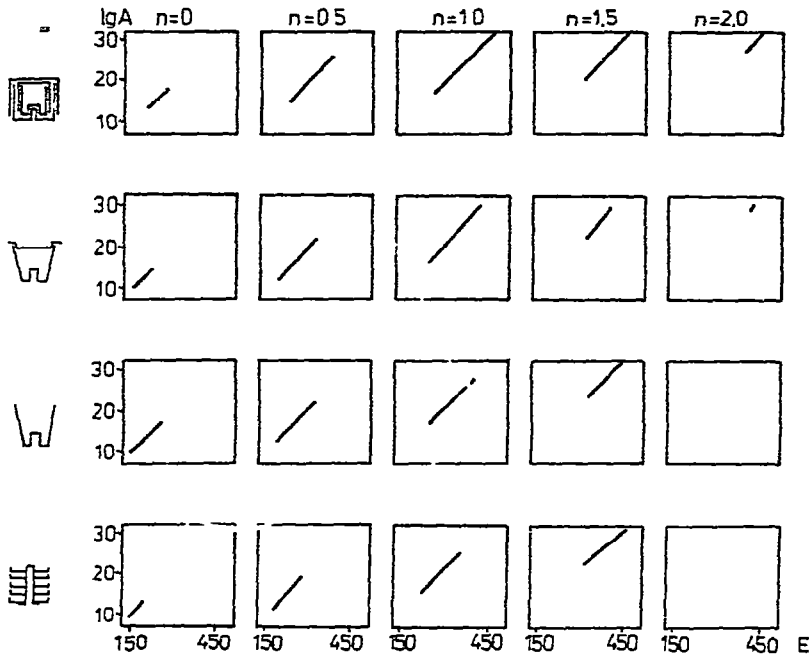Fig. 4. The confidence regions of the TG curve parameters for $Ca(OH)_2$.

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Fig. 5 The confidence regions of the TG curve parameters for Ca(COO)$_2$

to demonstrate schematically the change of confidence region of parameters A, E and n of the Arrhenius equation in cases where either the type of reaction or the type of sample holder has changed.

Considering the data contained in Figs. 3–5, it can be established that, in the case of the measured TG curves, the parameters of the Arrhenius model can be estimated only with great error, which is practically unacceptable. Comparing the extension of the confidence region obtained by the measured (Figs. 3–5) and simulated (Figs. 1 and 2) TG curves, it can be concluded that, in the case of measured curves, the uncertainty of estimation is considerably greater than in the case of simulated curves.

EXPERIMENTAL FACTORS INFLUENCING THE TG CURVES

In the case of non-isothermal thermoanalytical curves, reaction kinetic calculations based on the Arrhenius model involve a further problem in addition to the uncertainty of parameter estimation. Namely, it can be proved [1,7] that under conventional conditions of thermoanalytical examination, the course of reactions leading to equilibrium taking place between the solid and gas phase is directed first of all by various heat and gas transport processes depending on the applied experimental conditions (shape and size of sample holder, grain size, sample amount, compactness of sample, rate of heating, ventilation of furnace, etc.). Thus, according to practical observations, the course of thermoanalytical curves is characteristic of the experimental conditions rather than of the reaction itself [1,7].
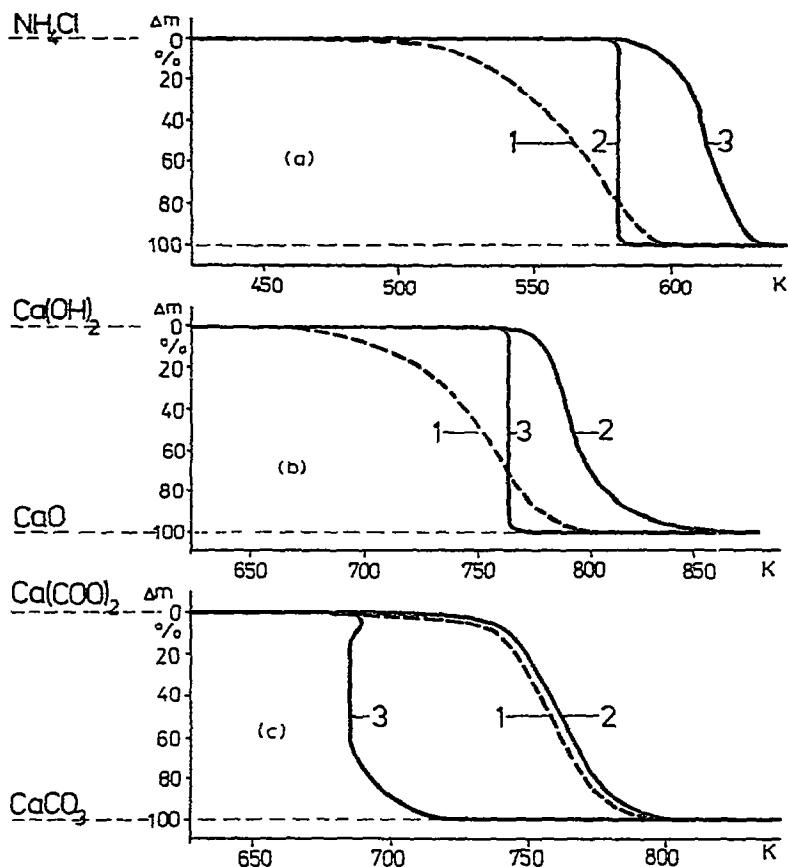
Fig 6 The effect of different experimental conditions on the thermogravimetric curves of NH₄Cl, Ca(OH)₂ and Ca(COO)₂

This is proved by Fig. 6, showing the thermogravimetric curves of the decomposition of ammonium chloride (a) calcium hydroxide (b) and calcium oxalate (c) made in open (curve 1) and labyrinth (curves 2 and 3) crucibles, with a dynamic heating program (curves 1 and 2) and quasi-isothermal quasi-isobaric measuring technique [1,7] (curve 3). Significant differences can be found among the courses of curves for which the differing experimental conditions are exclusively responsible.

Curves 1 were recorded in an open crucible, and consequently the partial pressure, as well as the decomposition temperature of the gaseous decomposition products, changed in an uncontrollable way during the whole transformation. The course of the curves was directed partly by gas transport and the actual conditions (e.g. compactness of sample) influencing it, and partly by the heat transport. In the case of dynamic heating, the sample having poor thermal conductivity is unable to take up instantaneously the heat necessary for its change. This has also contributed to the wide temperature limit of the course of curves 1.

In the case of curves 2, the course was influenced only by the slow heat transport due to the labyrinth crucible used. Namely, in this crucible, the partial pressure of the gaseous decomposition products reached atmospheric pressure early in the

course of transformation and remained constant. So, in this case. retardation of transformation can be explained simply by slow heat uptake.

The course of curves 3 recorded by quasi-isothermal quasi-isobaric measuring technique was influenced neither by heat, nor by gas transport, so the transformation took place at a well-defined constant temperature (quasi-isothermal). The use of a labyrinth crucible eliminates a change in the partial pressure of the gaseous decomposition products (quasi-isobar); the use of a quasi-isothermal heating technique [7] helps to eliminate the deformation effect of slow heat transport. The special heating mechanism built into the derivatograph ensures that the transformation takes place at a strictly constant rate. two orders of magnitude lower than the conventional one. It is to be noted that curve 3 of Fig. 6(c) does not show a constant decomposition temperature because the rate of decomposition is also dependent on the concentration [7].

A remarkable secondary proof in favour of the significant influence of the change in concentration of the gaseous decomposition products upon the decomposition process is the decomposition of calcium oxalate. This process leads to non-equilibrium [Fig. 6(c)] and took place both in open (curve 1) and labyrinth (curve 2) crucibles in a similar way and depended solely on the heat transport.

A consequence of the above facts is that, in the case of reactions taking place between solid and gas phases, the experimental conditions indirectly and the heat and gas transport processes directly influence the reaction to such an extent that all information regarding the reaction itself is masked. So, the course of TG curves is characteristic rather of the experimental conditions.

Based on the above facts. it can be concluded that the change in experimental conditions may cause a drastic change in the TG curves, e.g. even to a shift of 50–100 K on the temperature axis. which also makes parameter estimation illusory.

According to experience, when using the same instrument for recording the TG curves under similar conditions, the courses show only small differences. Uncertainty of reproducibility usually causes no problem if the curve is prepared for the purpose of qualitative or quantitative analysis or for discovering the thermal characteristics of the sample. However, a similar difference in the course of the curve makes the kinetic calculations impossible.

From the facts mentioned earlier, it is also clear that all attempts at standardization aiming to improve the reliability of kinetic calculations are in vain. The most detailed international standardization of experimental conditions would be useless since, although reproducibility would be improved, as regards the kinetic calculations. the errors belonging to the given conditions would only be fixed and not eliminated.

CONCLUSIONS

The parameters of the Arrhenius model can be estimated only with a quite large error, even in the case of simulated thermogravimetric curves, since the parameters

are dependent on each other and their joint confidence region is stretched. This uncertainty of parameter estimation further increases in the case of measured thermogravimetric curves. At the same time, however, in the case of heterogeneous reactions, the course of thermogravimetric curves is primarily influenced by the experimental conditions and not the reaction itself. Therefore, a change in experimental factors makes the interpretation of the estimated parameters impossible. Based on the above consideration, in the case of non-isothermal thermogravimetric curves for heterogeneous reactions, the Arrhenius model can be applied neither as an empirical nor as a theoretical model.

APPENDIX

1. Process being examined

The applicability of the Arrhenius model was examined on thermogravimetric curves of heterogeneous (solid–gas) thermal reactions accompanied by weight change and taking place under the influence of a dynamic (linear) heating program. The process examined is as follows

<p style="text-align:center">Experimental
conditions
↓</p>

Dynamic heating program →| thermal process |→ TG
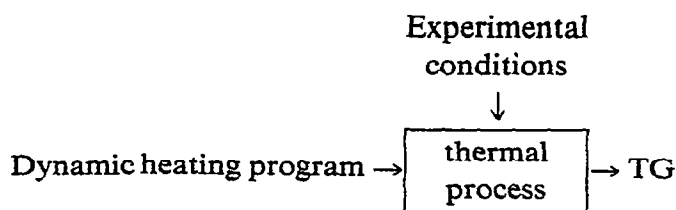
2. Arrhenius model

The so-called Arrhenius model describing the kinetics of heterogeneous, non-isothermal reactions demonstrates the progress of the reaction as follows

$$\frac{d\alpha(t)}{dt} = A \exp[-E/RT(t)][1 - \alpha(t)]^n \tag{1}$$

where A = pre-exponential factor (min^{-1}), E = activation energy (kJ mole^{-1}), n = order of reaction (dimensionless value), T = absolute temperature (K), t = time (min), R = universal gas constant (kJ mole^{-1} K^{-1}) and α = reaction coordinate (dimensionless value).

In the case of reactions accompanied by weight change, the reaction coordinate α is

$$\alpha = \frac{m_o - m_t}{m_o - m_v}$$

where m_o, m_t, m_v are the masses at the beginning, at time t, and at the end, respectively.

Using a linear heating program, the temperature depends on time according to

$$T(t) = T_o + Gt$$

where T = initial temperature (K) and

G = rate of heating (K min^{-1}).

Under certain conditions, instead of time temperature can be regarded as the independent variable in eqn. (1) and thus the following equation is obtained

$$\frac{d\alpha(T)}{dT} = A \exp(-E/RT)[1 - \alpha(T)]^n \qquad (2)$$

According to the earlier interpretation, the solutions $\alpha(t)$, or $\alpha(T)$ gained by integrating the differential eqn. (1) or (2), respectively are considered as "theoretical" TG curves.

3. "Good" model of physico-chemical processes

A mathematical model describing some kind of physico-chemical process can be regarded as a "good" one if it meets the following requirements: (a) the parameters of the model should have a well-defined physico-chemical meaning (b) there should be a one-to-one correspondence between the measured curve and the parameters estimated from the measured curve.

If only condition (b) is fulfilled, then the model is a good empirical one.

4. Measure of deviation of calculated and measured curves

If it can be supposed that the Arrhenius model is an adequate model of the process examined, then the solution curve, the so-called theoretical TG curve of the model, is the adequate model of the TG curve belonging to a given process. Several measures can be applied for characterizing the deviation between the measured and the theoretical, the so-called calculated TG curve, belonging to a given fixed parameter triplet A, E, n.

The discrete form of continuous TG curves has been used in our examinations. The deviation of curves has been evaluated by the average of squares of deviations S, i.e. by

$$S(A,E,n) = \sum_{i=1}^{N} \frac{1}{N}\left[TG^i_{measured} - TG^i_{calculated}(A,E,n)\right]^2 \qquad (3)$$

where index i represents the ith point of the discrete curve, $i = 1,\ldots N$.

5. Parameter estimation

The purpose of the kinetic calculations is the estimation of parameters A, E and n contained in model (1), or (2). Estimation of parameters of differential equations can be done in two ways: either by the differential or the integral methods. In our case, we applied the integration method, i.e. the solution of the Arrhenius model has been used for the calculation of the TG curve.
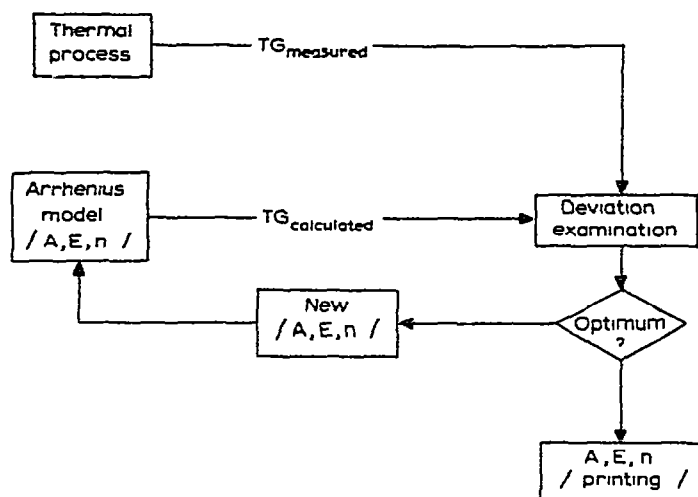
Fig 7 Logical structure of parameter estimation

Estimation of parameters of a given model means the optimization of parameter values according to the measure of deviation between the calculated and measured curves. Logical structure of parameter estimation is shown in Fig. 7.

For the optimization of the minimum of the deviation measure, the so-called "least-squares method", has been applied, i.e.

$$\min_{A,E,n} S(A,E,n) \tag{4}$$

The above optimization problem can be solved in various ways; in the course of our examinations, the so-called total enumeration was used. The principle of this method lies in the determination of the average of squares of deviations for all possible parameter combinations and then from among them the optimal one is chosen.

6. Goodness of model fitting

Since the measured results always involve errors, they can be regarded as stochastic variables, as can the estimated parameters, fluctuating at random depending on the measuring results. In addition to giving the estimated parameter values, the goodness of model fit and parameter estimation should also be somehow characterized.

For the characterization of model fit, the optimum value of the average of squares of deviations can be used, i.e.

$$\min_{A,E,n} S(A,E,n) = S(\hat{A},\hat{E},\hat{n}) \tag{5}$$

which is a measure of the deviation between the calculated and measured TG curves encountered even when choosing the "best" parameter values. The model fit can be called "good" if this optimum value of the average of squares of deviations is "small".

7. Goodness of parameter estimation

In addition to model fit, the goodness of parameter estimation can be characterized by, on the one hand, how a little fluctuation in the measured values changes the average of squares of deviations, and on the other, by how a great change is caused in the estimated parameter values by a small fluctuation in the average of squares of deviations, or inversely how the small fluctuation of parameters changes the average value of squares of deviations. The parameter estimation is regarded as good if the fluctuation of measured data (through that of squares of deviations) influences the estimated parameter data only to a small extent.

Goodness of parameter estimation can be characterized mathematically in several ways. In our present work, the effect of changing the TG curve and parameter values upon the value of average of squares of deviations is investigated.

8 Confidence region of parameters

The joint confidence region of parameters is defined as that region of space of parameters A, E, and n which contains all the parameter triplets of those TG curves calculated from them which do not deviate from the given reference (measured) TG curve by more than a given average value of the squares of deviations. The confidence region is limited by the minimum and maximum elements of parameter values belonging to the given goodness of fit. Any parameter triplet lying within these confidence limits can be considered as a parameter estimation of the measured curve being within the given goodness of fit.

9 Correlation of parameters

The shape of the confidence region allows some conclusions to be drawn concerning the correlation of parameters. The more stretched the shape of this hyper-ellipsoid region, the stronger the correlation among the parameters and the stronger the correlation among the parameters, the more ill-conditioned the problem of parameter estimation.

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