ROLE OF HEAT AND GAS TRANSPORT PROCESSES IN THERMAL ANALYSIS

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In the course of solid phase reactions heat and gas transport processes play a dominant role. Therefore, it would be necessary to standardize the experimental conditions which succeeded only in part with the elaboration of the simultaneous techniques. Likewise the two transport processes are responsible for the fact that on the basis of non-isothermal curves one cannot calculate kinetic parameters of the reactions. The quasi static-methods seem to be suitable for the elimination of the pernicious effect of these transport processes.

Keywords: gas/heat transport, kinetics, quasi static-methods

Introduction

The mechanism of solid phase reactions of type $AB_{(s)} \rightleftarrows A_{(s)} + B_{(g)}$ is composed of several elementary processes. Of these, the heat and gas transport predominate and push every other process characteristic of the reaction and material respectively into the background [1, 2]. However, the progress of heat and gas transport depends on the experimental conditions and so the shape of characterless curves changes from case to case causing much trouble to thermoanalysts in the course of time.

It caused difficulties e.g. in the interpretation and evaluation of non-isothermal curves. With the elaboration of simultaneous thermoanalytical techniques [1, 3, 4, 5] in other words, with the realization of the idea to measure the different variables (TG, DTG, DTA, EGA, TD etc.) in the very same sample the authors succeeded in standardizing the course of the different curves. However, this solved only the standardization of a single experiment. By changing the experimental conditions or by using different devices the question of standardization remained open.

The aim of the elaboration of the quasi-isothermal quasi-isobaric technique [1, 2, 6, 7, 8] was similarly the elimination of the pernicious effect of heat

and gas transport processes. With the help of this technique the heat and gas transport processes become normalized and lose their importance while the other elementary processes like nucleus formation, diffusion controlled or autocatalytic reactions etc. clearly manifest themselves in the curves offering valuable information on the transformations.

It is surprising that also the heat and gas transport processes are responsible for the fact that on the basis of non-isothermal curves it is not possible to perform kinetic parameter calculations.

Present paper analyses the common basis of these correlations.

Discussion

The practice of calculating reaction kinetic parameters began three decades ago, with the famous experiment of Borchardt and Daniels [9]. The mentioned researchers examined by means of a special DTA apparatus the decomposition of benzene diazoniumchloride. With the help of the Arrhenius model they calculated the kinetic parameters of the decomposition reaction. While they performed their experiments in solutions, i.e. in a homogeneous medium, their followers applied the method without restriction to the examination of solid phase reactions taking place between heterogeneous phases. Actually, that was the origin of the mistake.

These researchers left the fact out of consideration that Arrhenius made his observation by investigating reactions in solutions and gases respectively. This kind of reactions take place by the collision of molecules or ions. The mechanism of solid phase reactions is entirely different, as will be shown later. Consequently it is not to be expected ab ovo that for the latter case the very same correlation between reaction rate and temperature should be valid.

Many researchers only detected the great gap existing between theory and practice of the method but at the beginning they thought the cause of it lies in the unsuitability of the mathematical model. In the course of time many calculation methods had been developed in order to find a suitable model. Though since then most of the researchers gave up the hope even nowadays there are still who believe in it.

Authors at the Technical University in Budapest belonged from the very beginning to the sceptics and kept away steadily from publishing the results of such calculations. Under the pressure of cumulated proofs still in 1971 they denied 'expressis verbis' [6] the justification of parameter calculation under the mentioned conditions.

In Fig. 1 every TG curve illustrates the dissociation process of $CaCO_3$. These curves were obtained partly by applying the conventional non-isother-
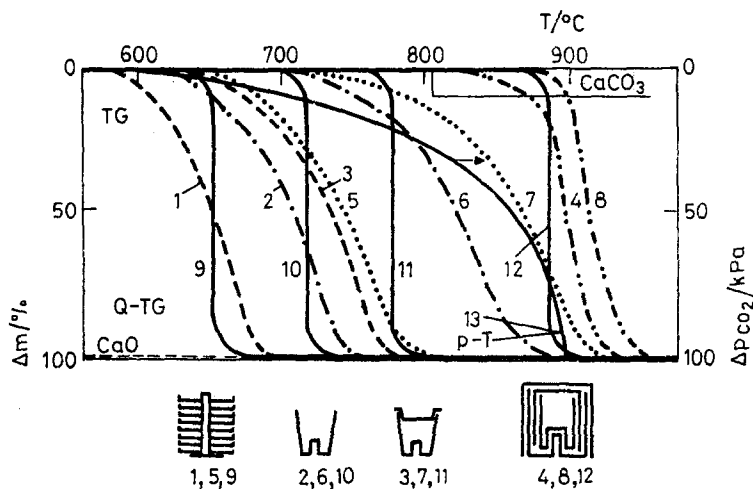
Fig. 1 Decomposition of CaCO₃ under different circumstances. Curves 1–8 (TG) examined under nonisothermal, curves 9–12 (Q-TG) under quasi-isothermal and quasi-isobaric circumstances. Heating rate: $2.5°C\ min^{-1}$ (curves 1–4) $10°C\ min^{-1}$ (curves 5–8). Rate of transformation: $0.5\ mg\ min^{-1}$ (curves 9–12). Weight of decomposition pressure of CO_2 and temperature

mal heating technique, partly by using the quasi-isothermal heating control, and by changing also the shape of the sample holders and the rate of the heating [2]. Table 1 contains the kinetic parameters, of curves 1–8, calculated by four well-known methods [10].

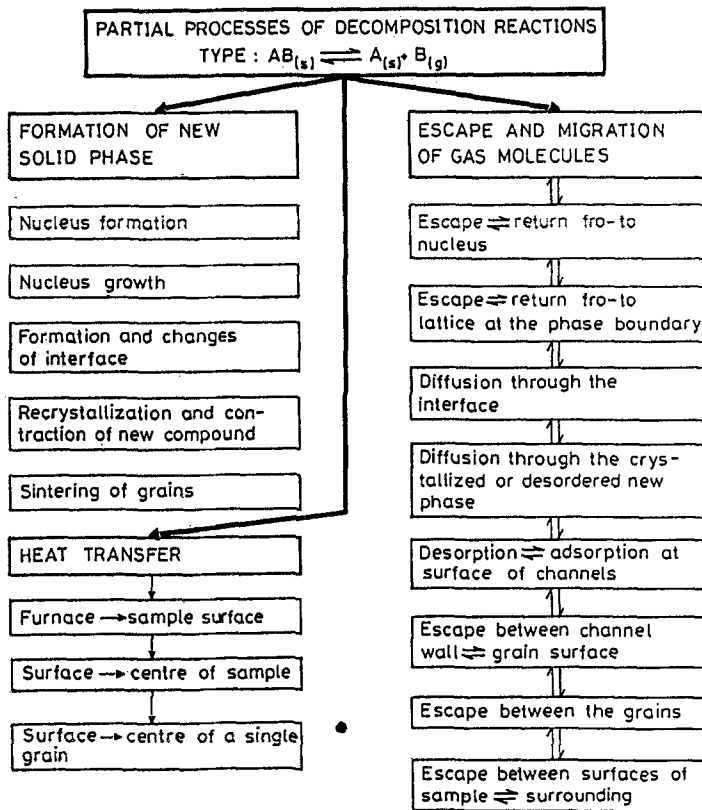Table 1 Kinetic parameters calculated with different methods

Sample-holder	TG curve	Kissinger	Freemann-Carrol		Horowitz-Metzger		Zsakó		
	No	n	n	E	n	E	n	E	A
〽	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	$2 \cdot 10^{14}$
_/	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	$7 \cdot 10^{13}$
⊔	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	54	$2 \cdot 10^9$
▣	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	$2 \cdot 10^{18}$

By comparing the shape of the curves and the values of the table the following questions may arise:

a) Why does the sigmoid shape of the TG curves change from case to case and why does it extend over a wide temperature range?

b) Why are the Q-TG curves of isothermal course?

c) Why do the characteristic temperatures of the curves change with the variation of the experimental conditions ?

d) Why do the values in Table 1 deviate?

We can find the answer to all the questions in Table 2; The elementary steps composing the whole transformation process are listed in this table [1, 2].

Table 2

PARTIAL PROCESSES OF DECOMPOSITION REACTIONS TYPE : $AB_{(s)} \rightleftharpoons A_{(s)} + B_{(g)}$	
FORMATION OF NEW SOLID PHASE	**ESCAPE AND MIGRATION OF GAS MOLECULES**
Nucleus formation	Escape $\rightleftharpoons$ return fro-to nucleus
Nucleus growth	Escape $\rightleftharpoons$ return fro-to lattice at the phase boundary
Formation and changes of interface	Diffusion through the interface
Recrystallization and con-traction of new compound	Diffusion through the crys-tallized or desordered new phase
Sintering of grains	Desorption $\rightleftharpoons$ adsorption at surface of channels
HEAT TRANSFER	Escape between channel wall $\rightleftharpoons$ grain surface
Furnace $\longrightarrow$ sample surface	Escape between the grains
Surface $\longrightarrow$ centre of sample	Escape between surfaces of sample $\rightleftharpoons$ surrounding
Surface $\longrightarrow$ centre of a single grain	

Let us outline the characteristic elements of the decomposition mechanism of a single grain of calcium carbonate. The transformation is introduced by nucleus formation as shown in Fig. 2. Nucleus formation and nucleus growth are actually rapid processes which sometimes begin with delay. After the nuclei have covered the whole surface of the grain, the phase boundary gradually becomes shifted towards the centre of the grain leaving

behind the 'inter face' layer. The chemical reaction in its strict sense i.e. the departure of the carbon dioxide molecule from the lattice and the rearrangement of the concerning part of the lattice take place first in the nuclei and later solely along the 'phase boundary'. This partial process is the most rapid of all the elementary processes. Since the performance of the transformation is always determined by the rate of the slowest process, therefore the course of the transformation of the sample is not influenced at all by the chemical reaction itself. However, from the point of view of parameter calculation just this would be of interest.
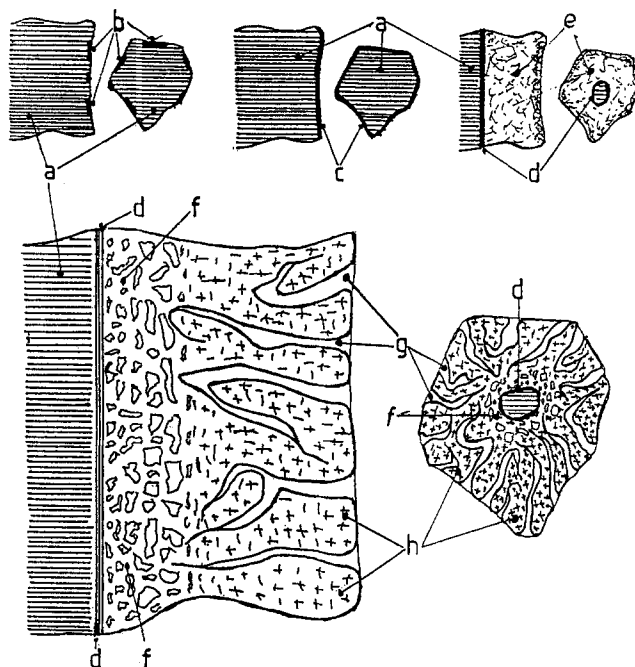
Fig. 2 Decomposition mechanism of a single CaCO₃ grain.
a) Original phase, b) nucleus, c) nuclei coating the grains, d) phase boundary, e) compact new phase, f) interface, g) channels, h)crystallized new phase

The gas molecules liberated from the lattice meet already at the beginning of their migration with difficulties. The gas molecules must namely diffuse with the ion-empty space mechanism through the interface layer consisting of disordered aggregates of microcrystallites.

Sometimes just this disorder makes the diffusion extremely difficult. To this process is due that in Fig. 3 the decomposition of manganese ammonium

phosphate monohydrate is protracted over several hundred degrees [2]. In this case the gas diffusion-resistance of the compact new phase (e in Fig. 2) was so strong that it pushed the influence of every other elementary process into the background. Consequently the resistance of the interface against gas diffusion can become rate controller of the reaction.

It is known that in most cases just like in the case of calcium carbonate this diffusion-resistance is small because the opposite outward layer of the interface becomes continually recrystallized.

The newly formed phase becomes sintered. First narrow capillaries are being formed which later widen to large channels. So, carbon dioxide has not to diffuse through the whole new phase but getting to the inner surface of one of the channels can escape still deep within the grain (Fig. 2).
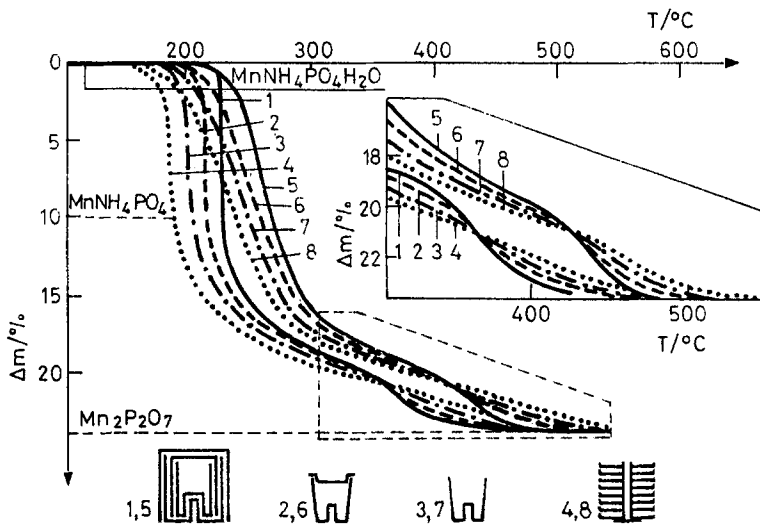
Fig. 3 Decomposition of $MnNH_4PO_4 \cdot H_2O$. 1–4 curves (Q-TG) traced under non-isothermal, 5–8 curves (TG) under quasi-isothermal and quasi-isobaric circumstances. Partial pressure of H_2O + NH_3 changed with the type of sample holders as follows, curves 1–4 and 5–8 respectively, ~100, 20, 5, 1 kPa

In general, the extent of the recrystallization of the new phase is strongly influenced by the experimental conditions. For example in the case of $MnNH_4PO_4 \cdot H_2O$ (Fig. 3) the porosity of the interface grew with the partial pressure of gaseous products. This follows from the fact that in the vicinity of 400°C the sequence of the TG and Q-TG curves changed for the reverse. This phenomenon can be explained by the reverse sign effect of the water and ammonia vapour exerted on the equilibrium of the reaction on one hand and on

the porosity of the interface, on the other. The curves came into existence as resultant of these two effects.

At this point have we arrived to the analysis of the source of every trouble, i.e. to the pernicious effect of heat and gas transport (Table 2).

The liberated gaseous products diffuse outwards from the sample through the space unfilled by grains, while air diffuses toward the centre continuously diluting the products. The stationary state corresponding to the experimental conditions would set in every case. The lowest temperature value at which the transformation can start at all and the highest one at which the reaction must end is defined by the correlation: decomposition pressure-temperature (curve 13 in Fig. 1). While the shape of the curves – within these limits – depends on the conditions of the gas diffusion, respectively in an indirect way on the experimental conditions. This is the explanation why curves 1–8 in Fig. 1 are shifted in phase and changed their shape in dependence of the applied sample holders, and of the rate of the applied heating.

By applying a non-isothermal heating program the sample of poor heat conductivity is not able to take up the great amount of heat with the rate dictated by the heating program and necessary to the progress of the reaction. Accordingly a temperature drop occurs within the sample. This does not need any further proof, since the measuring principle of DTA and DSC methods is based on this fact. It is to be noted that the expression 'temperature drop' covers very complicated and complex processes and so the analysis of them is to be neglected in the frame of this report.

Actually to this temperature drop can mainly be attributed that according to curves 1–8 in Fig. 1 the transformation took place more or less in a wide temperature interval.

In Fig. 4 the correlation is illustrated existing between the temperature drop within the calcium carbonate sample, the change in the partial pressure of the gaseous products, the temperature and weight changes and the location of the single grains by applying as well the conventional as the quasi-isothermal measuring technique.

As the left side of this figure shows, due to the temperature drop the transformation of the individual grains takes place in different time periods depending on the location, whether the grain is on the surface of the sample or in its centre. But in dependence of the location of the grains the course of the single transformations are also changing with the variation of the partial gas pressure.

If we accept the outlined picture of the transformation mechanism as a correct one, we may say that no physico-chemical sense can be attributed to kinetic parameters calculated on the basis of non-isothermal curves.

As a matter of fact this consideration led to the authors the development of the quasi-isothermal quasi-isobaric measuring technique [1, 2, 6, 7, 8].

This method can be characterized in a condensed form as follows. The heating controller system of the derivatograph automatically establishes between sample and furnace such a temperature difference which is necessary that the transformation should take place at an exceedingly low and strictly constant rate. As a result the reactions take place slower by orders of magnitude than reactions do in the case of conventional heating; therefore there is enough time for the sample to take up from the furnace the heat of the reaction. No temperature drop takes place within the sample. The distribution of heat stays homogeneous. Due to this in the grains, independently, whether they are situated in the centre of the sample or on the surface of it, the transformation begins and hours later ends practically at the same temperature as shown in the right side of Fig. 4.
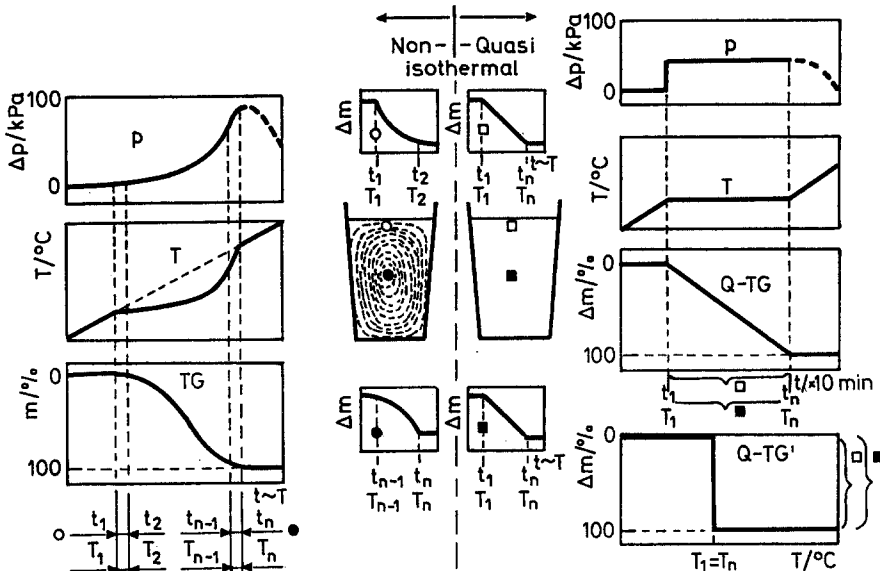

Fig. 4 Correlation between partial pressure (Δp), temperature (T), change in weight (Δm), temperature drop and location of the single grains within the sample holder in the case of decomposition of $CaCO_3$ under non-isothermal and quasi-isothermal quasi-isobaric conditions

To the spontaneous stabilization of the temperature contributes also that the heating controller with establishing a constant reaction rate in an indirect way automatically ensures also the constancy of gas formation. Since during the transformation, the experimental conditions, including temperature also, stay unchanged, the rate of the diffusion of the gaseous products and of air of

opposite direction does not change either. The partial pressure of the gaseous product respectively the sample temperature sets in at the value corresponding to the experimental conditions and stays constant up to the end of the transformation.

Therefore, the course of curves 9–12 of Fig. 1 is of quasi-isothermal character and therefore, the reaction took place in all the instances at the temperature corresponding to the partial pressure of carbon dioxide determined by the shape of the sample holder.

Many other similar examples could be demonstrated here. However, a significant part of inorganic compounds do not decompose in isothermal way, because from the normalized heat and gas transport processes such other processes take over the rate determining role which are much slower than the former ones. Such an example we could see in Fig. 3 or can be seen in Fig. 5
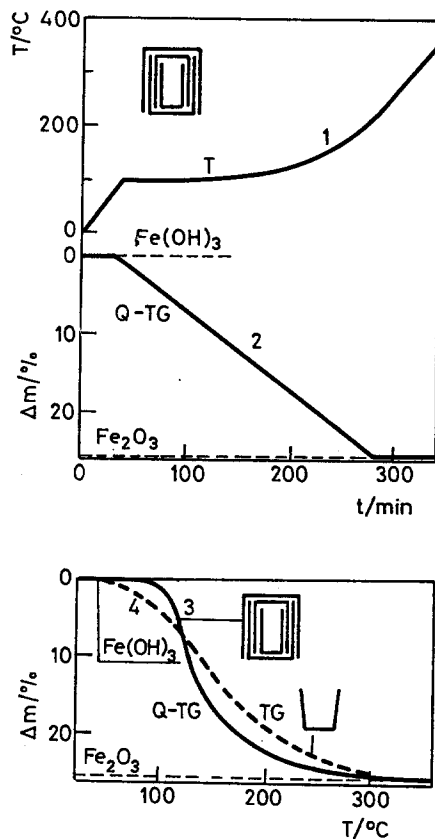

Fig. 5 Q-TG curves of iron(III) hydroxide as a function of time (2) and temperature (3) examined in labyrinth crucible. Conventional TG curve (4)

of the gel of iron(III)oxydehydrate. In the latter case towards the end of the transformation the remaining OH-groups of amorphous gel-like aquooxides composed of long chain molecules can split off only by a significant rise of temperature, because the distance between the untouched OH-groups increases and the steric hindrance grows. That is the cause on one hand why the course of the Q-TG curve in Fig. 5 is not isothermal. The other cause is the amorphous structure (Fig. 2).
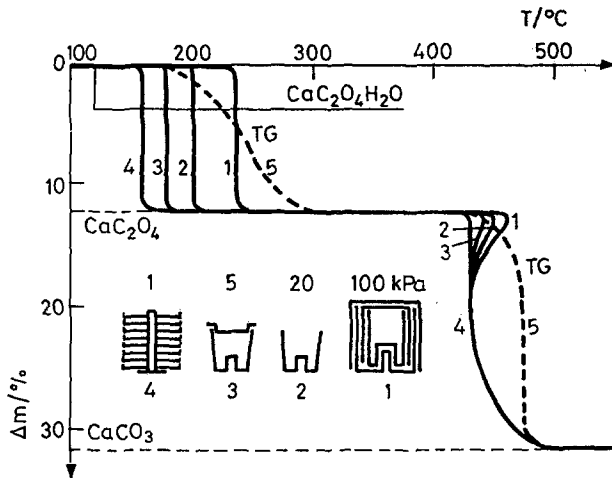

Fig. 6 Decomposition of $CaC_2O_4 \cdot H_2O$ under quasi-isothermal–quasi-isobaric (Q-TG) and non-isothermal (TG) conditions traced by different type of sample holders

Figure 6 shows the dehydration and decomposition of calcium oxalate monohydrate under non-isothermal and quasi-isothermal heating conditions and applying four different sample holders [2]. Based on the curves it can be stated that the dehydration led to equilibrium. This follows from the condition that the first section of the Q-TG curves was in all the four cases of isothermal course and that the single decomposition temperatures, became shifted in phase according to the partial pressures of gas product which depended on the shape of the sample holder.

We may also be sure that the decomposition of water-free calcium oxalate does not lead to equilibrium since the second steps of the four Q-TG curves are completely congruent and of anisothermal course.

The beginning of the second step of the Q-TG curves indicates a temporary overheating of the sample. Here the nucleus formation was hindered. That the heating controller should be able to establish the prescribed rate of weight changes it was necessary to increase automatically the temperature of

the sample. However, when a sufficient amount of nuclei already became formed the sample temperature became automatically reduced again in order to keep the rate of the decomposition at a constant value.

One may even guess the cause of the hindrance of nucleus formation from the magnitude of the bec shaped part of the curve indicating the overheating. Namely the extent of overheating corresponded with the partial pressure of the gaseous products being formed within the sample. It was the highest in the case of the labyrinth crucible and the lowest in the case of the multiplate sample holder. It is known that gas molecules adhering to the active points of the surface of crystals and blocking them may hinder the start of the decomposition. It is probable that in the present case either the carbon monoxide or the water molecules of the earlier gas product played this role.
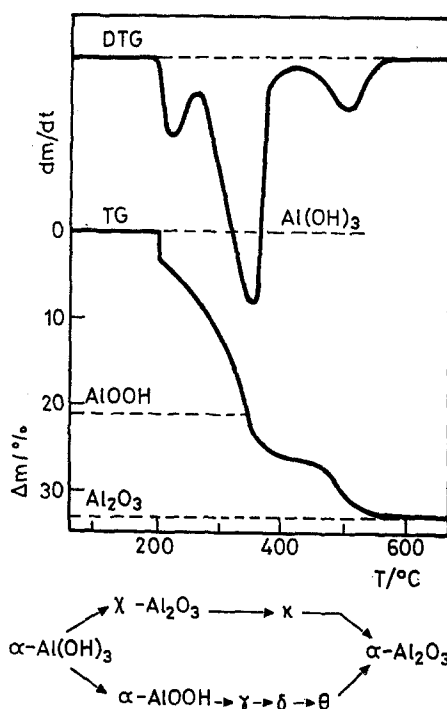

Fig. 7 Decomposition of gibbsite under conventional circumstances

With X-ray examination it was detected a long time ago that the decomposition of gibbsite may occur in two ways (Fig. 7). It decomposes either directly to aluminium oxide or indirectly under the formation of boehmite as intermediate. However, it was difficult to harmonize this perception with the

course of the conventional TG curve, although it already carried this informa-
tion in itself in a hidden way. In the Q-TG curves illustrated in Figs 8 and 9
this perception clearly manifests itself [7, 11] and X-ray examination (Fig. 10)
on the samples prepared by the course of quasi-isothermal heating proved
[11] the usefulness of the method.

In point a of the Q-TG curve started the delayed nucleus formation under
the formation of boehmite. Up to point b the temperature of the overheated
sample dropped and the boehmite-formation continued in an anisothermal
and non-equilibrium reaction which suddenly ended in points c-c'. Thereafter
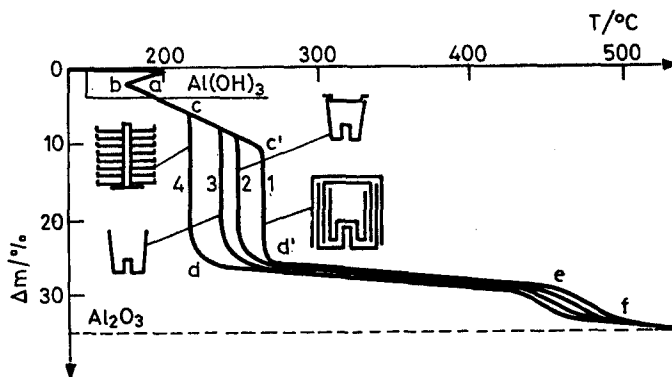a new isothermal reaction started leading to equilibrium which – in a com-

Fig. 8 Decomposition of gibbsite under quasi-isothermal–quasi-isobaric conditions (Q-TG).
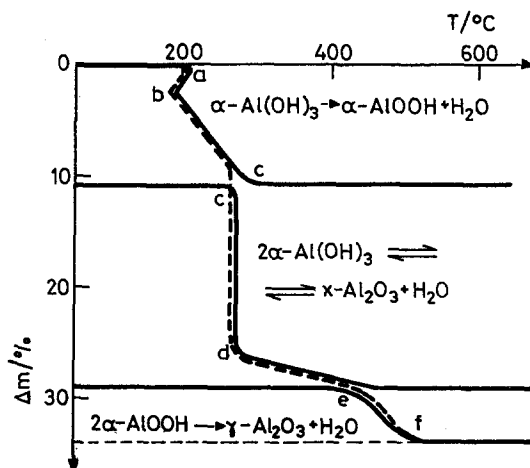Traced by using different types of sample holders

Fig. 9 Examinations of gibbsite after interrupting the heating. Curve 1: changes in the
amount of boehmite, curve 2: changes in the amount of Al_2O_3

petitive way – pushed the boehmite formation into the background. The gibbsite decomposed directly to aluminium oxide. In points d-d' also this reaction ended because the gibbsite ran out. The boehmite intermediate lost its water content between points e and f. The process was also leading to equilibrium.
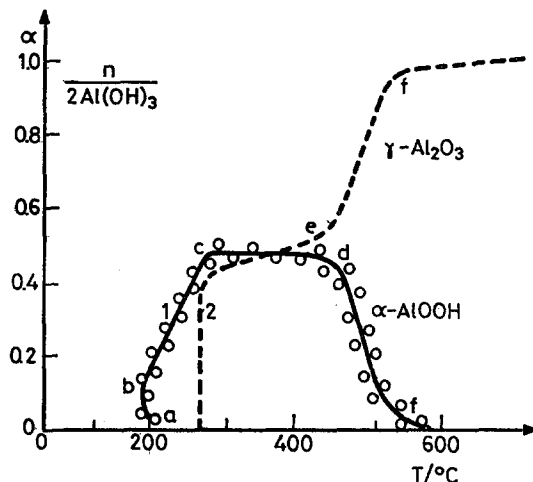

Fig. 10 Overlapping reactions of the decomposition of gibbsite

In the case of exothermal reactions the heating controlling system automatically governs the furnace temperature in a way that it should always be lower than the temperature of the sample. The magnitude of this difference ensures that the spontaneous exothermal reactions, should take place also very slowly and at a uniform rate. Figure 11 proves the fact that based on the feed-back principle, the reaction rate is really regulated by the transformation itself and not by the accumulated heat. Here the TG and Q-TG curves of nitrocellulose are shown [12]. As the course of these curves proves, the originally explosion like decomposition of nitrocellulose (curves 2, 4) can be regulated by means of the quasi-isothermal measuring technique in a way that it takes place in several hours (curves 1, 3).

When a technical or scientific problem is ripe enough for the solution, researchers nearly simultaneously even in the farest spots of the world may solve it independently from each other. This happened in the case of the quasi-static methods, too [8]. Authors built up their quasi-isothermal control-system in Budapest in 1964 [6, 13]. Using the 'feed back' principle this controller was governed by the reaction of the DTG signal, that measured the derivatograph with exactness. Nearly simultaneously Rouquerol [14] publish-

ed his measuring system which was similarly able to ensure that the transformation should take place at a very low and constant rate. In contrast to our solution Rouquerol governed the heating controller by a sensor which measured the pressure of the gaseous decomposition product in a way that the pressure should stay constant. He called his method 'Controlled transformation rate thermal analysis (CRTA)'. Bean and Oliver [15] let patented a control-system which was governed by the DTA signal. Due to the migration of the DTA base line this method did not stand the test. In 1977 Sørensen [16] started from the principle of the stepwise isothermal heating. He composed his heating program of countless isothermal sections.
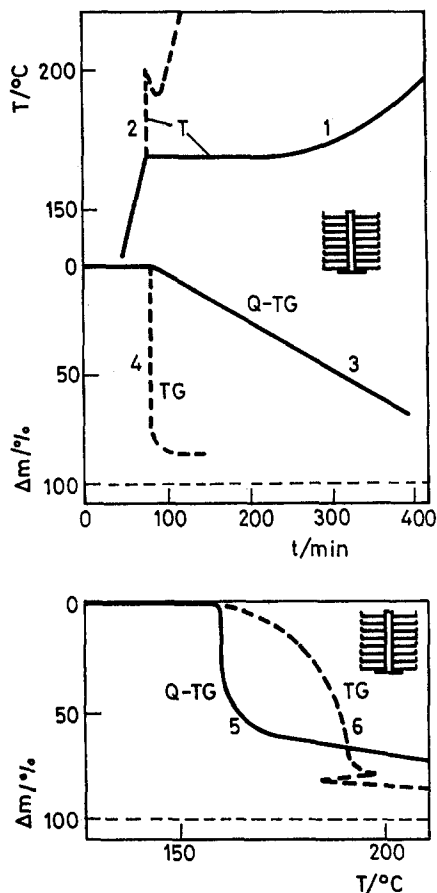

Fig. 11 Decomposition of nitrocellulose in N_2 atm under quasi-isothermal–quasi-isobaric (curves: 1, 3, 5) and non-isothermal (curves: 2, 4, 6) circumstances. Curves 1–4: traced as a function of time and curves 5–6: as a function of temperature

The listed measuring techniques agree with each other only in their intentions, while their measuring principles and results, too, are different. From the point of view of nomenclature we propose therefore to call the methods identical in their intentions uniformly 'quasi-static measuring techniques'. For the sake of distinction the name of the single methods should remain as they were originally called by their elaborators.

References

1 J. Paulik and F. Paulik, Simultaneous Thermoanalytical Examination by Means of the Derivatograph in Wilson-Wilson's Comprehensive Analytical Chemistry, Ed. G. Svehla, Vol. XII., Ed. W. W. Wendlandt, Elsevier, Amsterdam 1981.
2 F. Paulik and J. Paulik, J. Thermal Anal., 5 (1973) 253.
3 F. Paulik, J. Paulik and L. Erdey, Z. Anal. Chem., 160 (1958) 241.
4 F. Paulik, J. Paulik and L. Erdey, Talanta, 13 (1966) 1405.
5 F. Paulik and J. Paulik, Analyst, 103 (1978) 417.
6 J. Paulik and F. Paulik, Anal. Chim. Acta, 56 (1971) 328.
7 F. Paulik and J. Paulik, Thermochim. Acta, 4 (1972) 189.
8 F. Paulik and J. Paulik, Thermochim. Acta, 100 (1986) 23.
9 H. J. Borchard and F. J. Daniels, Amer. Chem. Soc., 79 (1957) 41.
10 M. Arnold, G. Veress, J. Paulik and F. Paulik, J. Thermal Anal., 17 (1979) 507.
11 F. Paulik, J. Paulik, R. Naumann, Köhnke and D. Petzold, Thermochim. Acta, 64 (1983) 1.
12 F. Paulik, J. Paulik and M. Arnold, J. Thermal Anal., 12 (1977) 383.
13 F. Paulik, J. Paulik and L. Erdey, Patents in: Austria, England, France, Germany, Hungary, Italy, USA (1962).
14 J. Rouquerol, Bull. Soc. Chim. Fr., (1964) 31.
15 C. M. Bean and R. H. Oliver, Patent in England (1964).
16 O. T. Sørensen, J. Thermal Anal., 13 (1978) 429.

Zusammenfassung — Beim Verlauf von Feststoffreaktionen spielen Wärme- und Gastransport eine wesentliche Rolle. Eine Standardisierung der experimentellen Bedingungen wäre deshalb erforderlich, was jedoch bisher nur bezüglich der Erarbeitung von Simultantechniken gelang. Außerdem sind diese beiden Transportprozesse dafür verantwortlich, daß man ausgehend von nichtisothermen Kurven keine kinetischen Parameter berechnen kenn. Quasistatische Methoden scheinen geeignet zu sein, um den störenden Einfluß dieser Transportprozesse zu eliminieren.