

THERMOANALYTICAL EXAMINATION UNDER QUASI-ISOTHERMAL–QUASI-ISOBARIC CONDITIONS

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ABSTRACT

The review begins with a short introductory survey on the history of the development of quasi-static measuring techniques. Thereafter, the authors give a detailed description of the measuring principles and theoretical fundamentals of the methods developed by themselves, of the so-called quasi-isothermal–quasi-isobaric (Q-TG and Q-TD) technique as well as of the simultaneous Q-TG/Q-DTG/Q-DTA and Q-TG/Q-TGT methods. Using examples, they demonstrate the characteristic types of the new kinds of curves and classify them according to their interpretation. With the presentation of a rather large amount of experimental material, the aim of the authors, beyond demonstrating the advantages of the methods, is also to express their disbelief in the justification of calculations of reaction kinetic parameters on the basis of dynamic thermoanalytical curves.

INTRODUCTION

Similar to physical processes, e.g. melting or change in modification on heating, in an ideal case chemical transformations leading to equilibrium should also take place at a defined temperature and in an isothermal manner, as shown by curves 1 and 2 in Fig. 1. In contrast, chemical transformations under dynamic heating and conventional experimental conditions would take longer and often be extended over a temperature interval of several hundred degrees, as shown by curve 3. It can be proved that in this case heat and gas transport processes are primarily responsible [1–4].

A sample of poor heat conductivity is not able to instantaneously absorb the necessary transformation heat, taking about 300 kJ mol^{-1} , and so the progress of transformations is primarily defined by the rate of heat absorption.

In the case of reactions leading to equilibrium with a prolonged reaction time, the partial pressure of the gaseous decomposition products inside open sample holders continuously increases from zero to atmospheric pressure during the transformation. Thus, the equilibrium of the reaction would continuously be shifted in an uncontrollable way towards higher temperatures [4].

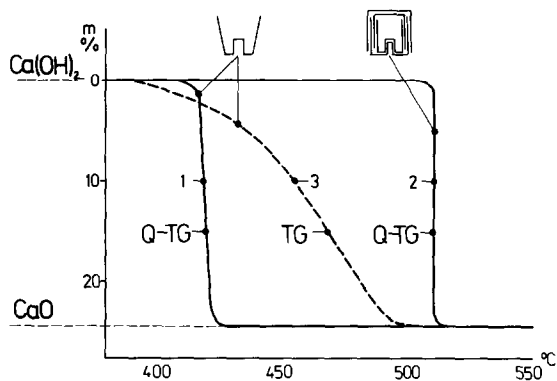


Fig. 1. Decomposition of calcium hydroxide [4] examined with quasi-isothermal (curves 1 and 2) and dynamic (curve 3) heating techniques in open (curves 1 and 3) and labyrinth (curve 2) crucibles.

In order to eliminate the distorting effect of these processes, more than twenty years ago the authors developed the quasi-isothermal–quasi-isobaric measuring technique.

HISTORICAL REVIEW

The initial step in the development of the whole family of quasi-static methods occurred in 1962 (Table 1) when the authors applied for patents first in their own country [5a] and later in another seven countries [5b]. The invention covered by these patents was a device (Fig. 2) made to perform thermogravimetric examinations under quasi-isothermal–quasi-isobaric conditions (Q-TG). The patent offices published the invention *ex officio* between 1965 and 1968. Although in the meantime the authors obtained a series of results using their home-made apparatus, due to delayed industrial interest (Q-Derivatograph) and the restrictions associated with business policy, the first scientific publication only appeared in 1971 [5c].

The measuring principle of the quasi-isothermal control system, initially built in the laboratory and later, in 1972, industrially (Hungarian Optical Works, Budapest, Q-Derivatograph), is demonstrated in Fig. 2.

The heating controller (4) of the deriving thermobalance (8) increases the temperature of the sample (1) in the conventional way (e.g. $3^{\circ}\text{C min}^{-1}$) as long as the weight of the sample is constant. As soon as a weight change begins and the weight reaches a given value, the light signal of the galvanometer (7) of the deriving system (12, 13) deviates and falls upon one of the double phototransistors (5). An electric signal immediately reduces the heating voltage with the intervention of the control system (4). Thereupon the temperature of the sample immediately decreases and, hence, so

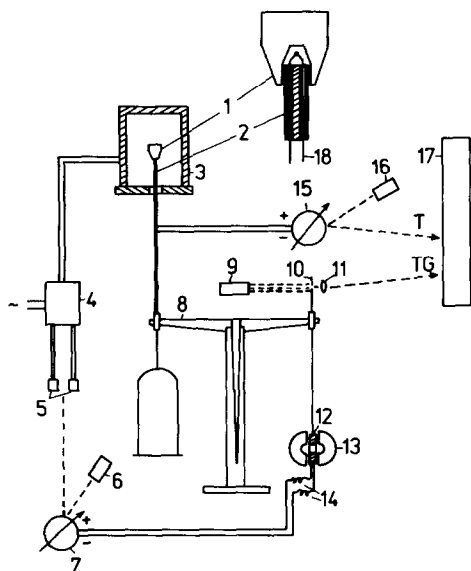


Fig. 2. Authors' apparatus for TG examinations under quasi-isothermal and quasi-isobaric conditions [5]. (1) Sample holder, (2) corundum tube, (3) furnace, (4) heating controller, (5) photo transistors, (6) lamp, (7), (15) galvanometers, (8) balance, (9), (16) lamps, (10) optical slit, (11) enlarger lens, (12) coil, (13) magnet, (14) flexible wire, (17) photopaper, (18) thermocouple.

does the rate of decomposition. The light signal of the galvanometer migrates from the phototransistor and the controlling mechanism brings the heating voltage back to the earlier value. This controlling cycle lasts for only a few seconds and is repeated over and over again until the end of the transformation. Thereafter, until the beginning of the next reaction the heating controller again increases the temperature at the former rate (i.e. $3^{\circ}\text{C min}^{-1}$). Using this technique the transformations take place at a very low and strictly constant rate (e.g. $dm/dt = 0.1\text{--}0.5 \text{ mg min}^{-1}$, $\Delta m = 100 \text{ mg}$).

Figure 3 shows the course of the decomposition of potassium hydrogencarbonate examined [5c] with the quasi-isothermal (curves 1–3) and the conventional (curve 4) heating techniques.

The following method, which can be classified as a quasi-static measuring technique, was published by Rouquerol [6] in 1963 (Table 1). He placed a mixture of cobalt sulphate hydrate and calcium hydroxide into a vessel (1 in Fig. 4) in vacuum ($1 \times 10^{-2} \text{ kPa}$). The temperature of the furnace (2, 3) was regulated with the help of a control system (4–8) sensitive to pressure changes, such that within the vessel the pressure remained low ($1 \times 10^{-2} \text{ kPa}$) and constant. The furnace temperature was measured and recorded (Fig. 5). Where a reaction has taken place, the temperature curve became horizontal. In this way Rouquerol [6] could define the transition temperatures more precisely.

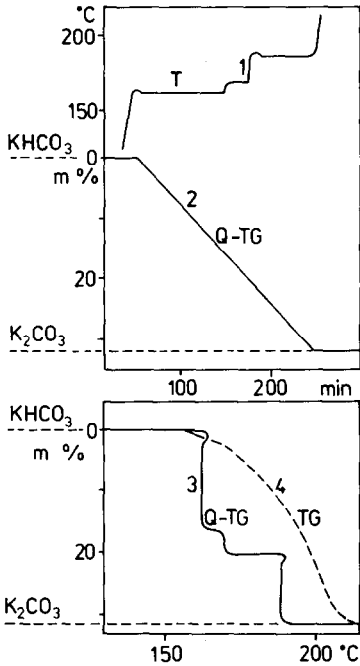


Fig. 3. Decomposition of potassium hydrogen carbonate under quasi-isothermal and quasi-isobaric conditions examined by the Q-Derivatograph [5c]. Temperature change (curve 1) and weight change as a function of time (curve 2) and temperature (curve 3) examined by quasi-isothermal (curves 1-3) and dynamic (curve 4) heating techniques using an open crucible.

In 1964 Bean and Oliver [7] had a device (Fig. 6) patented by means of which the temperature of transformations could also be measured more accurately than in the conventional way. They regulated the heating voltage

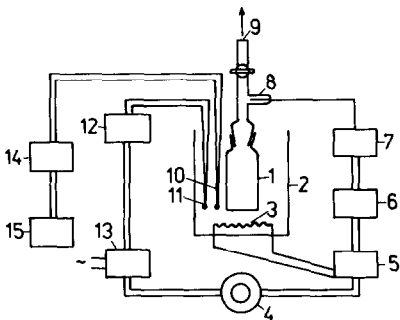


Fig. 4. Vacuum apparatus of Rouquerol for the determination of transformation temperature [6]. (1) Vacuum vessel, (2) furnace, (3) heating spiral, (4) autotransformer, (5) relay, (6), (12) controlling galvanometers, (7) Pirani gauge, (8) sensor of gauge, (9) join to the vacuum pump, (10), (11) thermocouples, (13) disjunctive, (14) recording galvanometer, (15) potentiometer.

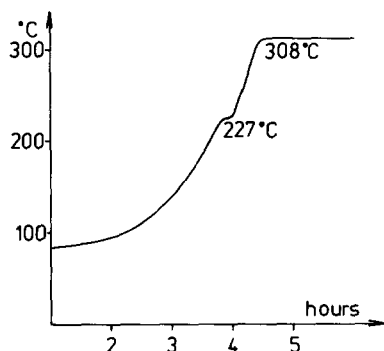


Fig. 5. Temperature change during the reaction between cobaltous sulphate monohydrate and calcium hydroxide at a constant and low (0.1 Torr) pressure according to Rouquerol [6].

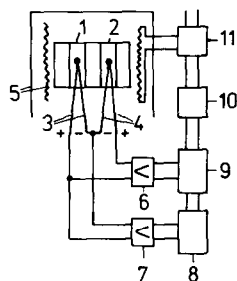


Fig. 6. DTA apparatus of Bean and Oliver for the determination of transition temperatures [7]. (1) Sample, (2) reference material, (3), (4) thermocouples, (5) heating spiral of the furnace, (6), (7) amplifiers, (8) recorder for tracing the temperature curve, (9) recorder tracing the DTA curve, (10) modular mechanism operated by recorder 9 for changing the heating resistance, (11) switcher.

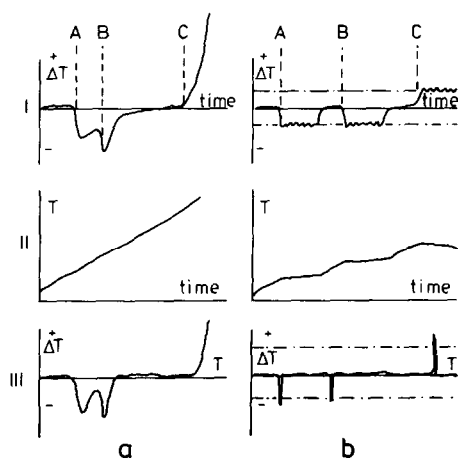


Fig. 7. Changes in temperature (II) and temperature difference as a function of time (I) and of temperature (III) examined with a conventional (a) and the patented (b) DTA apparatus of Bean and Oliver [7].

TABLE 1
Development of the quasi-static heating techniques

Ref.	Authors	Measured variables	Heating controlled by the signal	Patent		Publication	Received	Published
				Country	No.			
5a	Erdey, Paulik, Paulik	TG, T	dm/dt	Hungary	152 197		1962	1965
5b	Paulik, Paulik, Erdey			France	1 415 757		1964	1965
				Switzerland	415 116		1964	1966
				England	1 074 874	patent	1964	1967
				Austria	257 191	specification	1964	1967
				Italy	738 558		1964	1967
				U.S.A.	3 344 654		1964	1967
				F.R.G.	1 283 564		1964	1968
5c	Paulik, Paulik					1971	1971	
						Anal. Chim. Acta, 56 (1971) 328		
6	Rouquerol	T	dp/dt	-	-	Bull. Soc. Chim. Fr., (1964) 31	1963	1964
7	Bean, Oliver	T	Δt	England	1 063 898	patent specification	1964	1967
8a	Rouquerol	TG, T	dp/dt	-	-	Therm. Anal. Proc. 2nd ICTA	1968	1969
8b						J. Therm. Anal., 2 (1970) 123	1969	1970

9a	Paulik, Paulik	self-generated atmosphere												
9b														
10	Paulik, Paulik	TG, DTG, DTA, T	dm/dt	-										
11	Paulik, Paulik	TG, EGA, T	dm/dt	-										
12	Paulik, Paulik	TD, T	dI/dt	-										
13	Sørensen	TG, T	Δm	-										
14	Sørensen	TD, T	ΔI	-										

Hungary 163305
 France 7205857
 U.S.A. 3712110
 Italy 949160
 Switzerland 544939
 England 1388952
 Austria 343945
 F.R.G. 2206714
 Japán 1175888

patent
 specification
 Anal. Chim. Acta,
 60 (1972) 127
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 13 (1973) 253
 Anal. Chim. Acta,
 67 (1973) 437
 Therm. Anal., Proc.
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 (1977) p. 75
 J. Therm. Anal.,
 13 (1978) 429
 Therm. Anal., Proc.
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 (1980) p. 231

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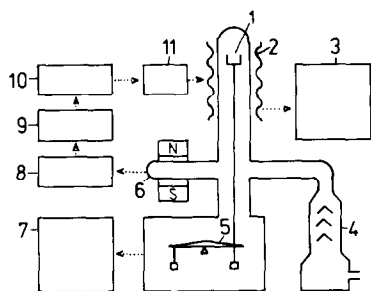


Fig. 8. Vacuum thermobalance of Rouquerol [8b] for Constant Decomposition Rate Thermal Analysis (CRTA) [8b]. (1) Sample, (2) heating spiral, (3) recorder for tracing furnace temperature, (4) vacuum apparatus, (5) vacuum thermobalance, (6) sensor of gauge, (7) recorder for tracing the weight change, (8) penning gauge, (9) pressure controller, (10) programmer motor, (11) heating controller.

of the furnace (5) of a DTA apparatus by means of an electromechanical construction (9, 10, 11). Thus, between the temperatures of the sample (1) and inert material (2) a temperature difference no greater than $\pm 0.5^{\circ}\text{C}$ should be established. For regulation, Bean and Oliver used the DTA signal and recorded the sample temperature (Fig. 7).

In 1968 Rouquerol [8a] suggested that his pressure-sensitive control system could be combined with a vacuum thermobalance. In 1969 [8b], he realized his idea (Fig. 8). Keeping the pressure of the gaseous decomposition products and the decomposition rate of the sample constant, he measured the weight change and furnace temperature. These curves were of similar character to the Q-TG curve of the authors of this paper with the difference that they gave information about transformations taking place in vacuum (Fig. 9). Rouquerol gave the name Constant Decomposition Rate Thermal Analysis (CRTA) to his method.

In 1971 the authors had three types of sample holder (Fig. 10) patented [9a], which were suitable for establishing a "self generated" atmosphere. Application [9b] of these sample holders ensured that transformations should take place in the presence of gaseous decomposition products at constant pressure (quasi-isobaric) on the one hand, and at atmospheric pressure (ca. 100 kPa) on the other (curve 4 in Fig. 14).

Since the first efforts had already been made to achieve quasi-isothermal heating with the Derivatograph, there was no technical hindrance to simultaneously recording, along with the Q-TG curve, Q-DTG and Q-DTA curves (Fig. 33) [10].

The next method developed by the authors [11] was simultaneous quasi-isothermal-quasi-isobaric thermogravimetry and thermogastitrimetry. According to this, beside the simultaneous measurement of weight changes, the gaseous decomposition products are quantitatively collected and absorbed in

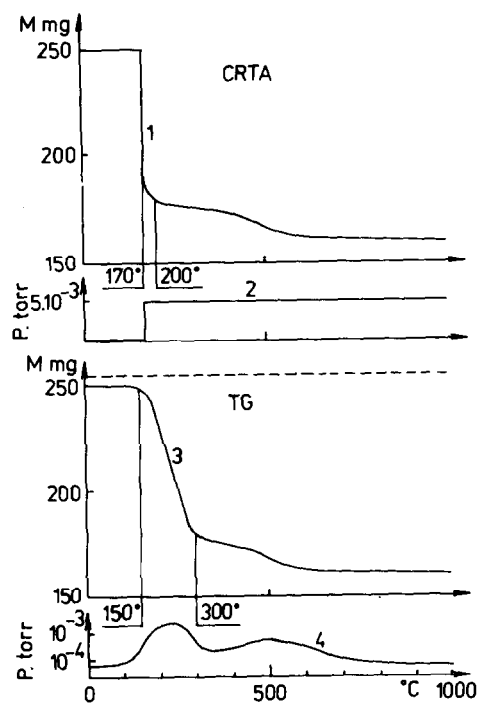


Fig. 9. Decomposition of gibbsite examined with the CRTA (Fig. 8) (curves 1 and 2) and conventional (curves 3 and 4) methods according to Rouquerol [8b]. Weight change (curves 1 and 3) and pressure change (curves 2 and 4).

water and one of the dissolved products is selectively and automatically titrated (Fig. 34). Heating control also takes place in this case with the help of the DTG signal.

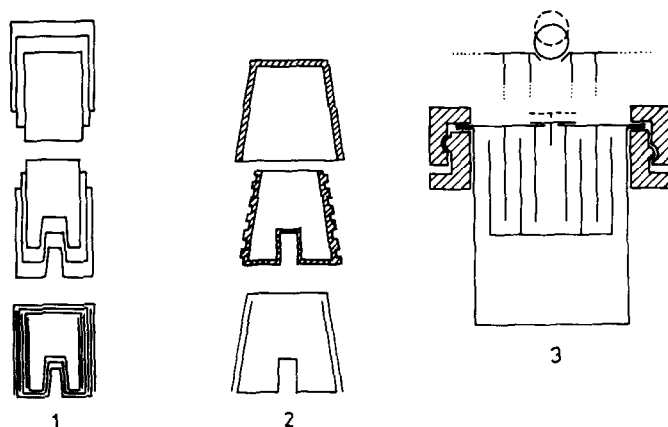


Fig. 10. Crucibles for realization of self-generated atmosphere constructed by the authors. (1) Labyrinth crucible, (2) conical crucible, (3) crucible with bayonet clutch and lamellar or ball vent [9a].

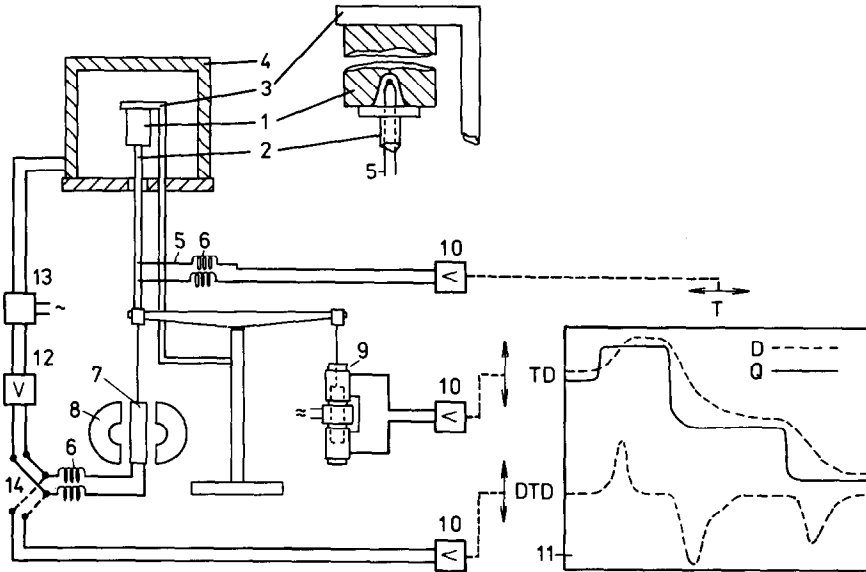


Fig. 11. Derivatograph for quasi-isothermal (Q-TD) and dynamic thermodilation (TD and DTD) measurements according to the authors [12]. (1) Test piece, (2) quartz tube, (3) quartz rod, (4) furnace, (5) thermocouple, (6) flexible conductor, (7) coil, (8) magnet, (9) differential transformer, (10) recorder, (11) chart, (12) controller for quasi-isothermal heating, (13) heating controller with thyristor, (14) switching device.

On the analogy of Q-TG measurements in 1977 the authors developed a method [12] for recording the thermodilation (TD) curve under quasi-isothermal–quasi-isobaric conditions (Q-TD). This can be performed after a small modification of the derivatograph (Fig. 11) which is already equipped with a quasi-isothermal heating controller. It is to be noted that in this case

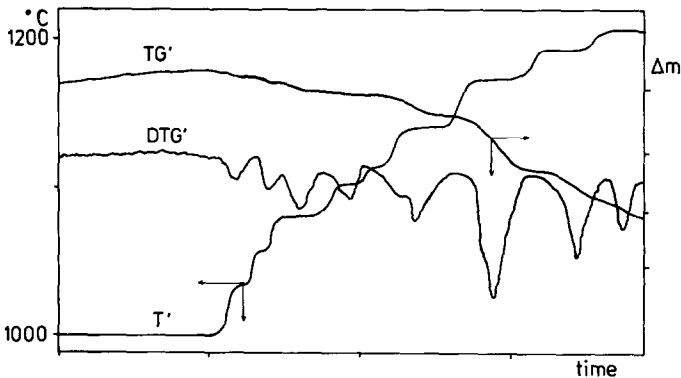


Fig. 12. Decomposition of CeO_2 in CO_2/CO atmosphere examined by the stepwise isothermal heating TG method of Sørensen [13].

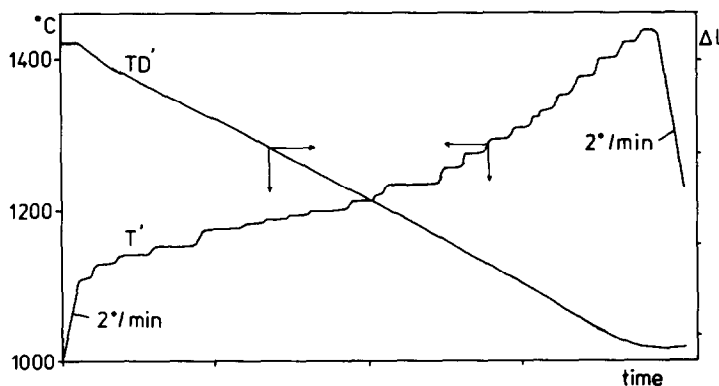


Fig. 13. Sintering of $\text{CeO}_2\text{-Gd}_2\text{O}_3$ (35%) mixture examined by the stepwise isothermal heating TD method of Sørensen [14].

not the weight but the length of the dilation body is measured (Fig. 35), and it is not the rate of the weight change but the rate of dilation (DTD) that controls the temperature changes such that the change in length should be very small and constant.

In 1978 Sørensen reported on another control system [13] which also uses the derived signal to control the heating of the sample. But in this system, which has been used both in thermogravimetric [13] and dilatometric studies [14], the heating is stopped when the rate of weight (or length) change is larger than a preset limit and the reactions thus take place isothermally, which is especially useful in kinetic measurements. Depending on the controlling mechanism the reactions can take place at one or at several temperature levels (steps) and in many cases enough data can be obtained in a single run to evaluate both the type of controlling mechanism and its activation energy. Figures 12 and 13 show examples of typical stepped temperature curves obtained in thermogravimetric and dilatometric measurements, respectively. In his early publications Sørensen also termed his method quasi-isothermal, but in his later publications he has used the term Stepwise Isothermal Analysis.

Neither measuring principles nor the results obtained by the techniques discussed are identical, they are only more or less similar. Nevertheless, all these techniques have a common characteristic feature in contrast with conventional dynamic and isothermal methods, viz. they permit transformations to take place at very low rates, practically in a quasi-static way.

Therefore, the authors propose to use “quasi-static methods” as a collective name, and in addition, for better differentiation, each individual technique could preserve the original name given by the author.

PRINCIPLES OF THE QUASI-ISOTHERMAL-QUASI-ISOBARIC MEASURING TECHNIQUE

The quasi-isothermal heating controller system incorporated in the Q-Derivatograph [10] worked initially [5] according to the principles illustrated in Fig. 2. Later [12] the roles of the galvanometer and phototransistors were taken over by an electronic relay-system (Fig. 11) which set in action the heating controller and immediately decreased the heating current voltage when the DTG signal reached the preselected limit value and increased it again when the latter dropped below this value. Recently, in the case of Derivatograph C [15], this operation was carried out by a microprocessor. Independent of its mode of operation from the heating controller system, however, such a difference is established between the temperatures of the furnace and the sample that the transformation should take place at a strictly constant and about two orders of magnitude lower rate (e.g. $dm/dt = 0.1-0.5 \text{ mg min}^{-1}$, $\Delta m = 100 \text{ mg}$) than that in the case of dynamic heating.

Owing to this special way of heating, simple reactions leading to equilibrium or changes of physical state (sublimation, boiling) take place without changing of the temperature of the sample (curves 1 and 2 in Fig. 1).

However, it must be emphasized that the heating controller system in question only regulates the rate of the transformation, and the setting in of the sample temperature at a value corresponding to the circumstances and temperature stabilization occur spontaneously.

However, the stabilization of sample temperature in reactions leading to equilibrium has one condition, viz. that the concentration of the gaseous decomposition products should remain constant within the sample, in the space between the grains, during the whole transformation process. This condition is also attained spontaneously.

The mentioned heating controller system ensures, with the stabilization of the transformation rate, that the gaseous decomposition products should be liberated at a constant rate.

Furthermore, soon after the beginning of the transformation an equilibrium is set up between the opposite diffusion processes of the gaseous decomposition products and the air if the sample is placed in an open sample holder.

It must also keep in mind that a strictly casual relationship exists between the ventilation conditions of the sample, i.e. the partial pressure of the gaseous decomposition products, and the transformation temperature and, therefore, with the possibilities of ventilation offered by the sample holders, the transformation temperature also changes proportionally. This is shown by curves 2-4 in Fig. 14.

Knowing the relationship existing between the decomposition pressure and temperature (curve 9), even the magnitude of the partial pressure of the

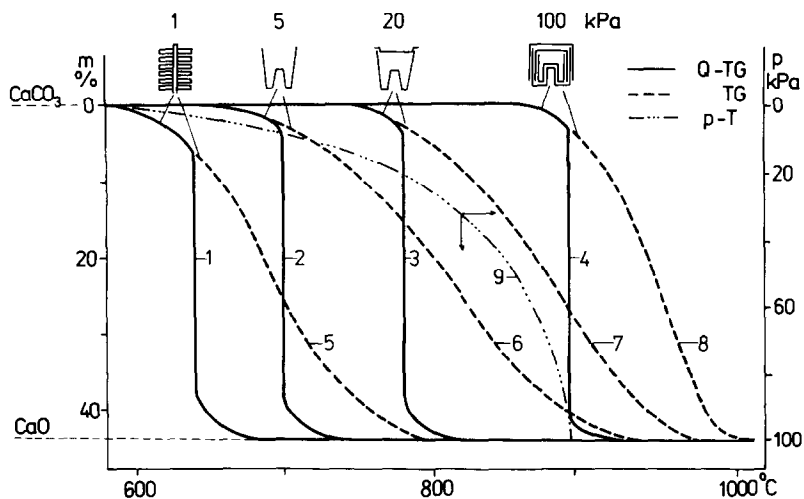


Fig. 14. Decomposition of CaCO_3 [10]. Sample holders: multiplate sample holder (curves 1, 5), uncovered (curves 2, 6), covered (curves 3, 7) and labyrinth (curves 4, 8) crucibles. Heating: quasi-isothermal (curves 1–4) and dynamic (curves 5–8). Correlation between decomposition pressure and temperature (curve 9).

gaseous product can be calculated with approximate accuracy. It was found [4], e.g. in the case of CaCO_3 (Fig. 14), that in the direct vicinity of the samples placed in the four various types of sample holder (multiplate sample holder, uncovered, covered and labyrinth crucible), the partial pressure of carbon dioxide was about 1, 5, 20 and 100 kPa, respectively.

From the point of view of equilibrium, quite special conditions are created by application of the so-called labyrinth, conical and ventily type crucibles, illustrated in Fig. 10. From the inside of these, immediately after the beginning of the reaction, air is expelled by the liberated gases and the gas streaming outwards through the narrow channel system prevents air from flowing backwards. Accordingly, in the inside of the crucible, a pure, “self-generated” atmosphere is being formed. Of the three types of sample holder, the labyrinth crucible provides the best seal. Simple transformations, which lead to equilibrium, would take place at a pressure corresponding to 100 kPa and at the so-called “normal transformation temperature”, known from physicochemistry. Curve 2 in Fig. 1, and Curve 4 in Fig. 14 were obtained by using this sample holder. On the basis of these curves, it can be stated that the “normal decomposition temperature” of $\text{Ca}(\text{OH})_2$ is 510°C , and that of CaCO_3 is 890°C .

In contrast, reactions not leading to equilibrium due to various factors emerging, like the decreasing concentration of the sample retarding diffusion of the gaseous products with increasing thickness of the new solid phase, etc., would slow down or even stop at a constant temperature. In the case of this type of reaction only with a continuous and sufficient increase in sample

temperature (curve 1 in Fig. 18) can the reactions be ensured to take place at an unchanged rate. This is also regulated by the transformation itself, with the intermediation of the heat controller system fully automatically based on the "feed-back" principle in a self-regulating way.

The performance of this type of reaction is not influenced by the concentration change of the gaseous products.

Although in the case of reactions not leading to equilibrium the sample temperature changes (curve 1 in Fig. 18) but exceedingly slowly ($1-10^{\circ}\text{C h}^{-1}$). Thus, in these cases one cannot speak of isothermal conditions, however, for quasi-isothermal conditions, it still applies. These considerations led the authors to designate their heating technique as a quasi-isothermal one.

RESULTS AND DISCUSSION

The conventional thermoanalytical curves give only stereotype and distorted pictures on the course of the transformations. The cause of this lies in heat and gas transport processes, the course of which changes according to experimental conditions from case to case [2-4]. As a result these curves are often more characteristic of the experimental conditions than of the transformation itself (Fig. 14).

The examples to be presented may serve as arguments that by means of the quasi-isothermal and quasi-isobaric measuring techniques the heat and gas transport processes can be standardized so that their pernicious effects can be eliminated. As a consequence of this the effect of further elementary processes can also manifest themselves in the formation of the curves. Accordingly, the finer details of kinetics and mechanism of reactions, hidden in the conventional curves, reveal themselves.

It was necessary to establish a system for classifying the processes which motivate the different forms of the Q-TG curves. The main types of transformations are schematically illustrated for memotechnical purposes in Tables 2-6.

According to the course of the Q-TG curves one may distinguish between two basic types of transformations. The conversion may take place without any temperature change, isothermally (Table 2d), or at a gradual temperature increase, non-isothermally (Table 2e).

Among the isothermal types of transformation can be found reactions which lead to equilibrium, such as dehydration of salt and metal complex hydrates [1-4,16-37], dehydroxylation of metal hydroxides [1,2,4,32,33], dissociation of ammonium salts [1,4], decomposition of metal carbonates and hydrogencarbonates [1-4,5c,9b,11,16,17,26,38,39] of metal sulphates or hydrogen ammonium sulphates [4,17,40], metal ammine complexes [2-4,16,18], and boiling of saturated solutions [4,26,30,31,35,36,41].

TABLE 2

type of reactions		Q-TG	
simple			a
consecutive	not overlapping		b
	overlapping		c
isothermal			d
non-isothermal			e

TABLE 3

influence of gas product exerted upon		Q-TG	
reactions	leading to equilibrium		a
	not leading to equilibrium		b
delayed nucleus formation	no influence		c
	influence		d

TABLE 4

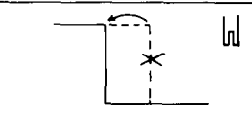
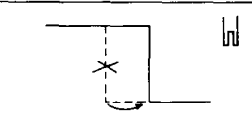
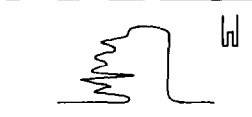
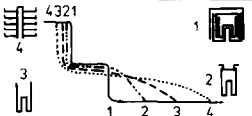
influence of foreign gases and solid contaminants		Q-TG
promoting effect	on the reaction	 a
delaying effect		 b
blocking effect upon sites causing different activities		 c
causing porosity changes in the new phase		 d

TABLE 5

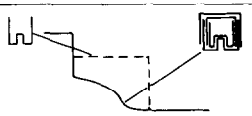
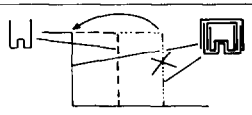
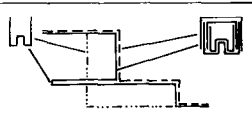
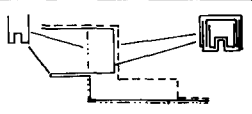

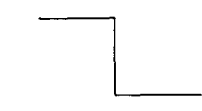

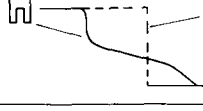
influence of gas product causing changes in reaction mechanism	Q-TG
secondary reaction	 a
new reaction	 b
with memory effect	 c
without memory effect	 d

TABLE 6

chem. and phys. processes in liquid phase		Q-TG	
change in reaction mechanism			a
boiling point changes	in saturated solution		b
	in not saturated solution		c
crust formation			d

Belonging to the group of non-isothermal types are those transformations which, due to one reason or another, do not lead to equilibrium, such as the dehydration of salt hydrates in the case of crust formation on the sample surface [31,34–36,41], dehydroxylation of metal hydroxides [1,2,32,33,42], decomposition of metal hydrogen or ammonium phosphates [2–4,18,20,21, 31,43], decomposition of metal complexes [37,41], decomposition of organic materials [2–4,16,27,44–46], decomposition of minerals with dislocations and foreign ions in the lattice [1,38–40,47], and boiling of unsaturated solutions [4,29,35,36,41,46].

A list of compounds investigated by the quasi-isothermal technique is given in Table 7.

Based on the shape of the Q-TG curves it can be stated that, for example, the dehydroxylation of $\text{Ca}(\text{OH})_2$ [1,4] (curves 1 and 2 in Fig. 1), the decomposition of CaCO_3 [1,3,4,16] (curves 1–4 in Fig. 14), the sublimation and dissociation, respectively, of NH_4Cl [1,42] (curves 1–4 in Fig. 15), and boiling or evaporation of water [35] (curves 1–4 in Fig. 16), were simple processes leading to equilibrium (Table 2a) which, under the given conditions, took place isothermally (Table 2d).

Figure 17 shows the Q-TG curve of the dehydration process of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as a function of time (curve 2) and of sample temperature (curve 3), respectively [1,4,47]. According to these curves the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ first lost two moles, then another two moles, and finally one mole of water. The two

TABLE 7

Compounds investigated by the quasi-isothermal technique

Compound	References	Compound	References
CaCO ₃	1-4, 9b, 16	CaSO ₄ ·2H ₂ O	3
K ₂ CO ₃ ·1.5H ₂ O	1, 19	CoSO ₄ ·7H ₂ O	22
KHCO ₃	1-4, 5c, 11, 15	CuSO ₄ ·5H ₂ O	17, 47
NaHCO ₃	4, 11	Fe ₂ (SO ₄) ₃	40
AlCl ₃ ·6H ₂ O	28	MgSO ₄ ·7H ₂ O	30, 34
BaCl ₂ ·2H ₂ O	4, 19, 27, 48	Cu(NH ₃) ₄ SO ₄ ·H ₂ O	4, 18
CoCl ₂ ·6H ₂ O	26	FeNH ₄ (SO ₄) ₂ ·12H ₂ O	1, 4, 47
MnCl ₂ ·4H ₂ O	19	Fe(NH ₄) ₂ (SO ₄) ₂ ·6H ₂ O	1
NH ₄ Cl	1, 4	CdNH ₄ PO ₄ ·H ₂ O	4, 20
Ni(NH ₃) ₆ Cl ₂	2-4, 16, 34	CoNH ₄ PO ₄ ·H ₂ O	4, 20
CaBr ₂ ·6H ₂ O	4, 46	MgNH ₄ PO ₄ ·6H ₂ O	4, 18, 21, 46
AgNO ₃	42	MgNH ₄ PO ₄ ·H ₂ O	4, 20, 46
Ca(NO ₃) ₂ ·4H ₂ O	35, 36	MnNH ₄ PO ₄ ·H ₂ O	2-4, 20, 34, 42
Ni(NO ₃) ₂ ·6H ₂ O	49	Ca(H ₂ PO ₄) ₂ ·H ₂ O	43
Ca(OH) ₂	1, 4	Ca(H ₂ PO ₄) ₂ ·H ₂ O + KCl	43
Fe(OH) ₃	1, 4, 47	Mg(H ₂ PO ₄) ₂ ·H ₂ O	43
Mg(OH) ₂	1, 4, 47	Mg(H ₂ PO ₄) ₂ ·H ₂ O + KCl	43
CaHPO ₄ ·2H ₂ O	31	H ₂ O	35
Na ₂ HPO ₄ ·2H ₂ O	31	Fe ₂ O ₃ + ZnO	4, 48
NaH ₂ PO ₄ ·H ₂ O	31	boemite	47
Na ₂ H ₂ P ₂ O ₇	34	calcite + vapour	39
Ca ₂ EDTA·7H ₂ O	25	calcite + NaCl	38
Cu ₂ EDTA·4H ₂ O	25	dolomite	1, 17
MgCdEDTA·9H ₂ O	4, 23	dolomite + vapour	39
MgCoEDTA·6H ₂ O	24	dolomite + NaCl	38
MgCuEDTA·6H ₂ O	24	gibbsite	2, 32, 33
MgMnEDTA·9H ₂ O	23	kaolinite	47
MgNiEDTA·6H ₂ O	24	magnezite	29, 39
Mg ₂ EDTA·9H ₂ O	23	magnezite + vapour	39
MnCuEDTA·6H ₂ O	24	magnezite + NaCl	29
Mn ₂ EDTA·9H ₂ O	23	pyrite	40
Zn ₂ EDTA·6H ₂ O	4, 25	CaC ₂ O ₄ ·H ₂ O	2-4, 15, 16, 34, 48
Ca(NO ₃) ₂ ·CO(NH ₂) ₂ ·H ₂ O	37, 41	nitrocellulose	4, 27, 45-47
FeS	40	1-oxy-2-diazonaphthalene-5-sulphochloride	4, 44, 46

first processes, examined using the dynamic heating programme (curve 4), nearly completely overlapped. In the Q-TG curve the two processes are unanimously separated despite the fact that between their transformation temperatures only a difference of 10°C exists. The two first consecutive processes (Table 2b) are isothermal (Table 2d) while the departure of the last water molecule is non-isothermal (Table 2e). In many cases it succeeded in separating the overlapping reactions with similar good results [1,3,11,16,19,22-26,29-32].

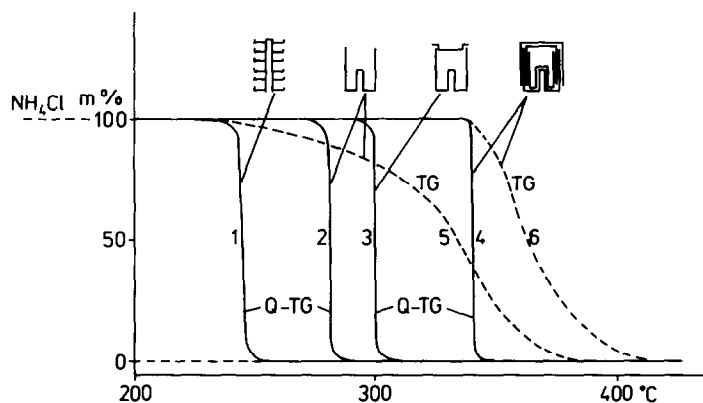


Fig. 15. Sublimation and dissociation, of NH_4Cl [1]. Sample holders: multiplate sample holder (curve 1), uncovered (curves 2, 5), covered (curve 3) and labyrinth (curves 4, 6) crucibles. Heating: quasi-isothermal (curves 1–4) and dynamic (curve 5).

Figure 18 shows the decomposition process of an amorphous $\text{Fe}(\text{OH})_3$ gel as a function of time (curve 2) and of sample temperature (curve 3), respectively [1,4]. According to the Q-TG curve the decomposition took place non-isothermally (Table 2e). It can be supposed that the water loss of the precipitate occurs in many consecutive (Table 2c) elementary polycondensation processes. Initially, the escape of water could easily occur from the hydroxyl groups situated near to one another in the neighbouring molecules. But with the progress of polycondensation, water could only escape from hydroxyl couples situated further and further apart, and the steric hindrance required for this demanded a larger and larger heat energy.

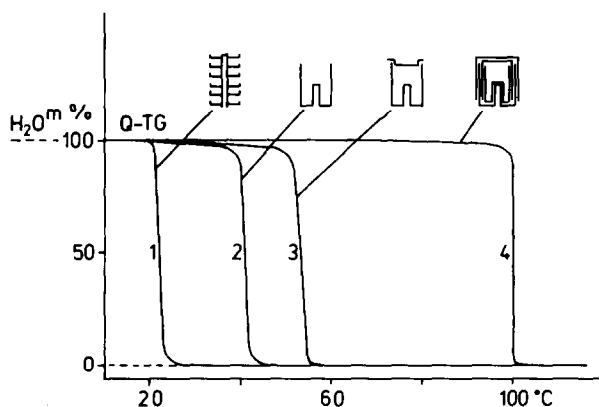


Fig. 16. Evaporation and boiling of H_2O [35]. Sample holders: multiplate sample holder (curve 1), uncovered (curve 2), covered (curve 3) and labyrinth (curve 4) crucibles. Heating: quasi-isothermal (curves 1–4).

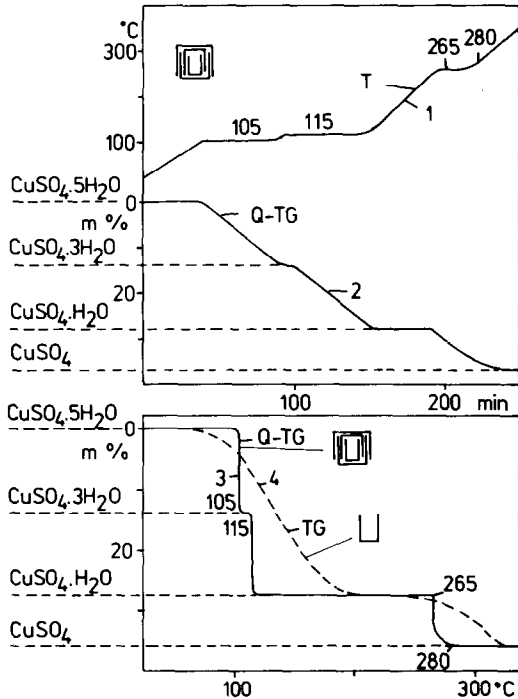


Fig. 17. Dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ [17]. Temperature change (curve 1) and weight change as a function of time (curve 2) and temperature (curves 3, 4) examined by quasi-isothermal (curves 1–3) and dynamic (curve 4) heating techniques using labyrinth (curves 1–3) and open crucibles (curve 4).

Therefore, in order to ensure that the reaction should take place at a constant rate the heat controller system had to increase the temperature of the sample continuously (curve 1 in Fig. 18).

From the Q-TG curves in Fig. 19 useful information can be obtained. This shows the dehydration of calcium oxalate monohydrate and decomposition of the anhydride intermediate [2,3,15,16,42,48]. These transformations were examined by using four different types of sample holder. It has already been mentioned that in the direct vicinity of the samples placed in the four types of sample holder the partial pressure of the gaseous product decreases in order to about one fifth of its original value.

If the reaction leads to equilibrium, due to exchanging the sample holders, the course of the single curves would be shifted in phase (Table 3a); in the reverse case the curves would coincide (Table 3b), as the first and second stages of decomposition of calcium oxalate (Fig. 19) prove.

As a rule it can also be accepted that if in the initial stages of the curve a transitional overheating is indicated by the appearance of a peak (Table 3c), then this can be attributed to a delayed nucleus formation [3,4,11,18,20,21,32,39]. If, for one reason or another, nucleus formation is delayed, this

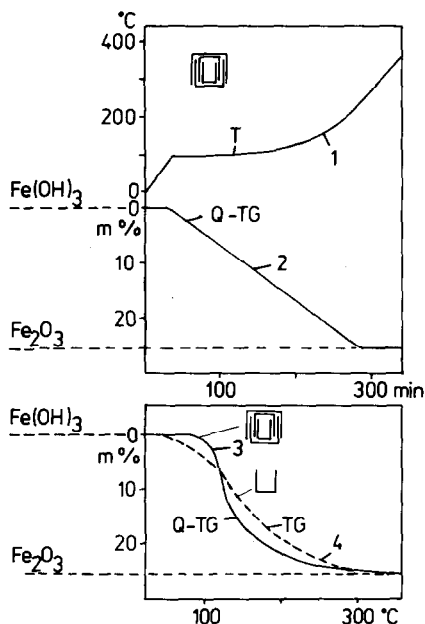


Fig. 18. Dehydration of $\text{Fe}(\text{OH})_3$ precipitate [1]. Temperature change (curve 1) and weight change as a function of time (curve 2) and temperature (curves 3, 4) examined by quasi-isothermal (curves 1–3) and dynamic (curve 4) heating techniques using labyrinth (curves 1–3) and open crucibles (curve 4).

would begin at a higher temperature than the transformation. However, if a sufficient amount of nucleus has been formed, then the temperature would drop spontaneously, because a lower temperature is sufficient for the trans-

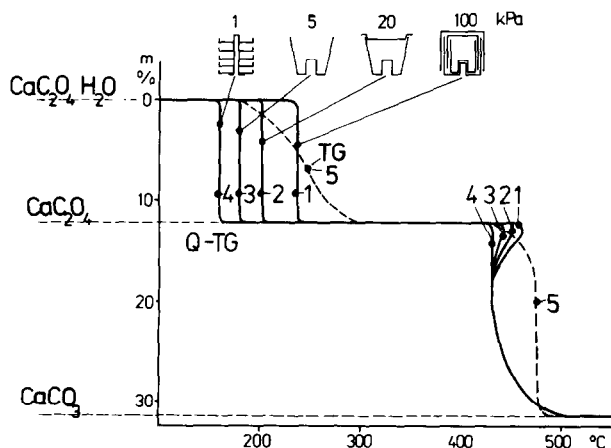


Fig. 19. Decomposition of the $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ [3]. Sample holders: multiplate sample holder (curve 1), uncovered (curve 2), covered (curve 3) and labyrinth (curve 4) crucibles. Heating: quasi-isothermal (curves 1–4).

formation to take place at the preselected rate. In accordance with this, it can be stated on the basis of Fig. 19 that the decomposition of water-free calcium oxalate was introduced by a delayed nucleus formation.

It even may be stated that in the present case [3,4] nucleus formation was delayed by carbon monoxide, liberated during the course of decomposition (Table 3d). From the Q-TG curve it can be unambiguously seen that a correlation exists between the concentration of carbon monoxide accumulated in the vicinity of the sample and the delaying effect which increases in direct proportion to the former. The extent of overheating was the largest in the labyrinth crucible (curve 1), while on the multiplate sample holder it did not occur at all (curve 4).

A probable explanation of this phenomenon is as follows. Active sites formed on the surface of crystals greatly influence the beginning of transformations. On the other hand, the gaseous decomposition product may either block or, in contrast, activate these active sites, thus delaying or accelerating the reaction. In the present case, the carbon monoxide blocked the active sites, which were on the surface of the calcium oxalate crystals.

Foreign gaseous or solid compounds can exert similar promoting (Table 4a) or delaying (Table 4b) effects, not only on nucleus formation but also on nucleus growth, in other words, on the whole transformation.

The Q-TG curves in Fig. 20 illustrate, for example, the decomposition of pure dolomite (curves 2 and 4), and that of a dolomite sample containing on its surface 2% of sodium chloride (curves 1 and 3). Both samples were examined [29] by using an open and a covered crucible. The large decrease in decomposition temperature caused by this small amount of contaminant is a warning to be careful when examining mineral substances, since these are never originally pure.

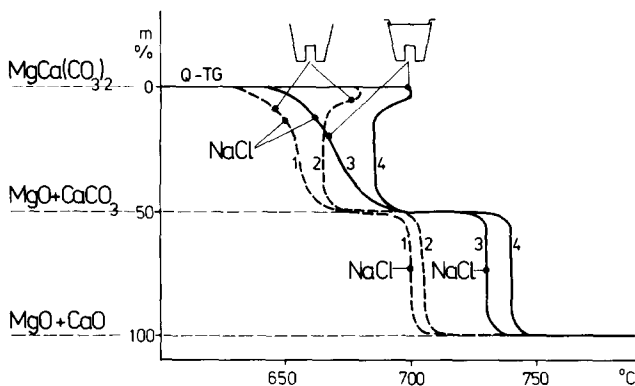


Fig. 20. Decomposition of pure dolomite (curves 2, 4) and of dolomite sprayed with 2% NaCl (curves 1, 3) [38]. Sample holders: Open (curves 1, 2) and covered (curves 3, 4) crucibles. Heating: quasi-isothermal (curves 1-4).

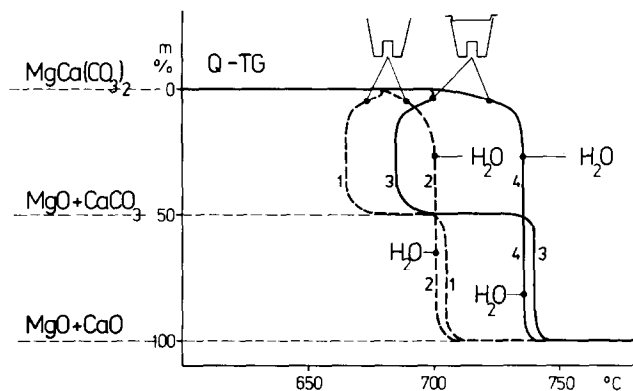


Fig. 21. Decomposition of dolomite in dry (curves 1, 3) and water-vapour saturated (curves 2, 4) N_2 atmospheres [39]. Sample holders: open (curves 1, 3) and covered (curves 2, 4) crucibles. Heating: quasi-isothermal (curves 1–4).

However, a phenomenon not widely known is that the small amount of water vapour present in air can block the active sites of the crystals, thus hindering (Table 4b) the decomposition of certain substances while it can also activate them, promoting (Table 4a) the decomposition of other materials. The Q-TG curves in Fig. 21 illustrate the dissociation of the earlier dolomite sample, taking place partly in a dried nitrogen atmosphere (curves 1 and 3), and partly in nitrogen saturated with water vapour (curves 2 and 4). According to these curves the initial period of decomposition is hindered, while the second is promoted by water vapour [1,39].

In certain cases these active sites may greatly differ in their activity (Table 4c). With DTA examinations it was earlier observed, for example, that under given conditions the oxidative decomposition of metal sulphides took place unevenly, its rate increasing and decreasing several times periodically. This phenomenon was explained by the existence of sites of strongly differing activity.

The authors also studied this phenomenon [40] with the Q-TG technique and found that by using the quasi-isothermal measuring technique the process can be detected very sensitively as Fig. 22 proves. The curves of this figure shows the oxidative decomposition of iron(II) sulphide in O_2 atmosphere and in air using different kinds of sample holders. As the Q-TG curves show the oxidation of iron(II) sulphide (eqn. 1) took place periodically over a broad temperature interval between 300 and 500°C. Erratic changes in the curves prove that site of various activities initiated oxidation at various times and at various points in the sample. From the grain containing the nucleus which began the process, the reaction would spread to the neighbouring grains without initiating conversion of the whole sample, because this due to certain causes (e.g. loose contact) would sooner or later stop. Thereafter the partial process will again be started by further

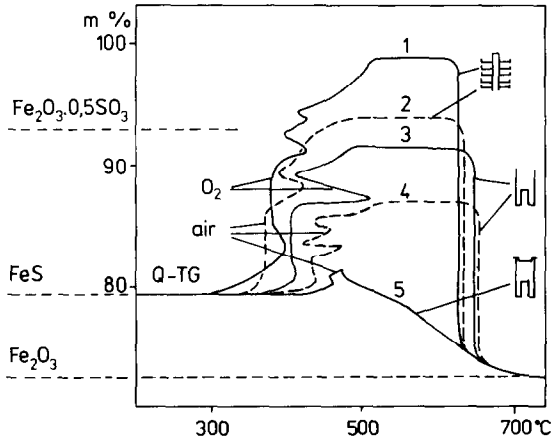
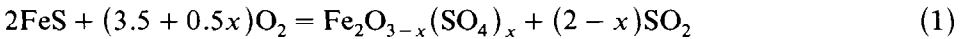


Fig. 22. Decomposition of FeS in the presence of O_2 (curves 1–3) and in air (curves 2, 4, 5) [40]. Sample holders: multiplate sample holder (curves 1, 2), open (curves 3, 4) and covered (curve 5) crucibles. Heating: quasi-isothermal.

nuclei whose activity with rising temperature, or due to other causes (e.g. departure of the blocking gas molecules), would meanwhile increase.

The dissociation of the intermediate $Fe_2O_{3-x}(SO_3)_x$ (eqn. 2) took place isothermally (Table 2d).

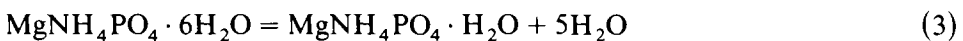


There may be several reasons why a reaction does not take place isothermally (Table 2e).

Organic compounds [3,4,41,44,45] do not decompose isothermally (Fig. 32), presumably because with the progress of transformation newer and newer intermediate products are being formed which are always more heat resistant than the former ones.

As seen from the example of $Fe(OH)_3$ (Fig. 18) with the progress of polycondensation reactions the liberated gaseous products must be formed because of hydroxyl groups becoming further and further apart. This steric hindrance may cause a rise in decomposition temperature.

If the transformation is composed of several more-or-less overlapping partial reactions of different transformation temperatures, the resultant temperature of the whole process would increase with the progress of the reaction [2–4,20,31,34]. The extent of overlapping, of course, also influences the resultant temperature. This phenomenon was observed on the example of $MgNH_4 \cdot PO_4 \cdot 6H_2O$ [4,18,21,46] (Fig. 23). During the course of decomposition of $MgNH_4 \cdot PO_4 \cdot 6H_2O$, the following partial reactions may take place



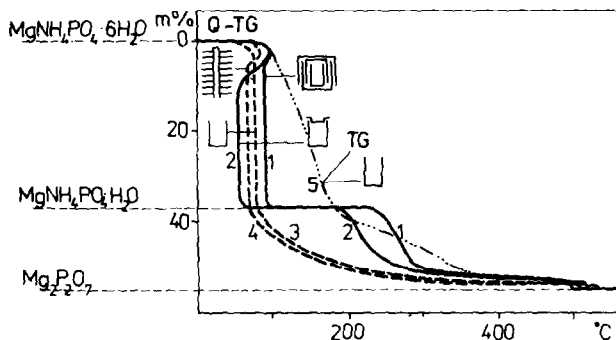
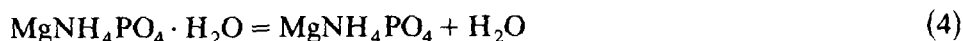


Fig. 23. Decomposition of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ [18,21]. Sample holders: labyrinth (curve 1), covered (curve 2), open (curves 3, 5) crucibles and multiplate sample holder (curve 4). Heating: quasi-isothermal (curves 1-4) and dynamic (curve 5).



Authors, by varying the applied sample holders, i.e. by changing the partial pressure of the gaseous decomposition products, shifted with tendency to the above partial reactions in phase and as a result (Fig. 23) obtained an irregular sequence of the curves (curves 1-4). This proved indirectly that the above statement is correct. This example also proved that several of the partial reactions listed above were originally reactions leading to equilibrium.

The decomposition of metal ammonium phosphates was investigated by X-ray and infrared techniques and it was found that the new crust-like phase formed on the surface of the grains is not porous as in most cases, but compact. Therefore, even reactions leading to equilibrium may become non-isothermal. With the progress of transformation the thickness of this crust continuously increases, and hence the departure of the gaseous decomposition products becomes more and more difficult, requiring increasing amounts of energy.

The fact that the last section of the decomposition (Fig. 24) of $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ [4,20,46] and other metal ammonium phosphates [2-4,20,34,46] extends over a wide temperature interval also seems to indicate that the formation of such a compact crust really does play a role in the decomposition process of these compounds.

The supposition of such a compact crust formation also seems to be justified by the observation of the authors [4,20,46] that in the cases of $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ and other metal ammonium phosphate hydrates [1,4,20,21,46] there is a correlation between porosity of the crust and concentration of the gaseous products (Table 4d). As it can be seen from

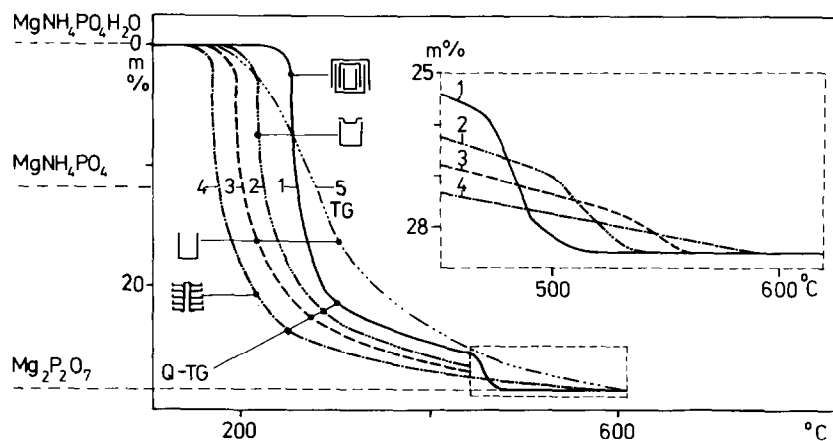


Fig. 24. Decomposition of $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ [20]. Sample holders: labyrinth (curve 1) covered (curve 2), open (curves 3, 5) crucibles and multiplate sample holder (curve 4). Heating: quasi-isothermal (curves 1–4) and dynamic (curve 5).

Fig. 24 the sequence of the Q-TG curves in the beginning corresponded to increasing partial pressure of the gaseous product formed within the applied sample holder, as a sign that the transformation leads to equilibrium (Table 3a). However, in the vicinity of 450°C the curves cross one another and their sequence changes to just the reverse. In the labyrinth crucible the transformation even ended at 500°C . In contrast, on the multiplate sample holder the conversion was protracted up to 600°C .

If the sample holders are exchanged, the reaction mechanism of the transformation also changes. The concentration changes of the gas product often drive the transformation in another direction, e.g. between solid and gaseous decomposition products secondary reactions (Table 5a) may take place, as the example of copper tetrammine sulphate monohydrate shows [18].

According to curve 2 in Fig. 25 the material lost water at 130 and 150°C and ammonia at 260 and 310°C if an open crucible was used. At 700°C the copper sulphate also decomposed in two steps. In contrast, the course of curve 1 proves that in the labyrinth crucible the transformation took place in another way. Since at 300°C ammonia is very reactive and it remained in the more closed sample holder for a longer time in contact with copper sulphate, it split off sulphur trioxide from the compound and formed ammonium sulphate with it.

By examinations carried out using various types of sample holders, it is found that the curves obtained do not follow one another in the sequence expected, i.e. in accordance with the partial pressure of the gaseous product. Authors observed this, for example, in connection with the decomposition of calcium hydrogen phosphate dihydrate [31]. According to Fig. 26 the first stage of the dehydration appeared in the case of the labyrinth crucible at a

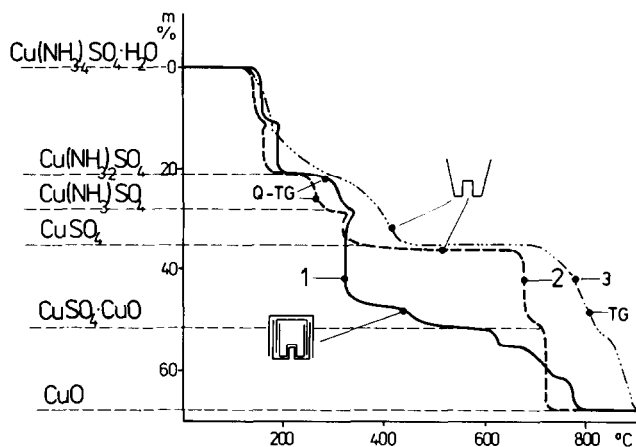


Fig. 25. Decomposition of $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ [18]. Sample holders: labyrinth (curve 1) and open (curves 2, 3) crucibles. Heating: quasi-isothermal (curves 1, 2) and dynamic (curve 3).

temperature about 50°C lower than by using the multiplate sample holder. This contradiction means that the reactions took place according to a different mechanism in these cases (Table 5b). Here it can be supposed that although in both cases non-stoichiometric apatite was formed, the elementary processes of the transformation and the composition of the intermediate products were different.

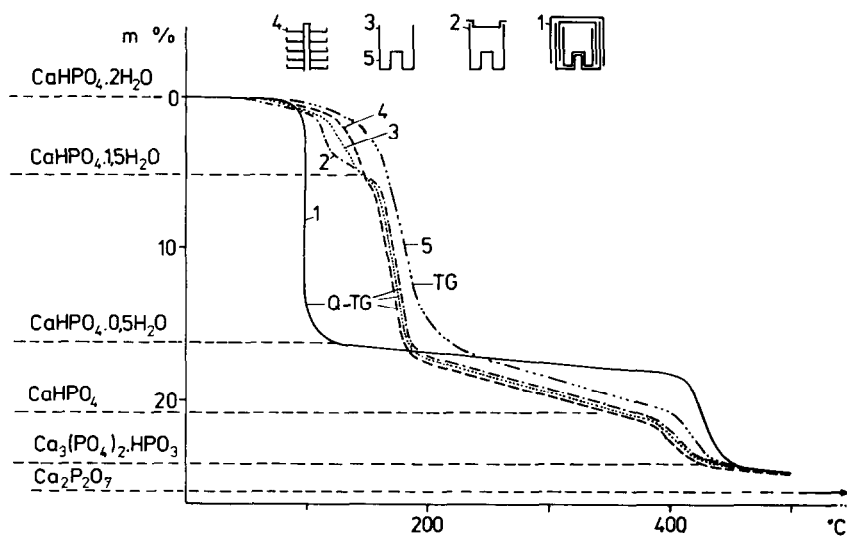


Fig. 26. Decomposition of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ [31]. Sample holders: labyrinth (curve 1), covered (curve 2), open (curve 3, 5) crucibles and multiplate sample holder (curve 4). Heating: quasi-isothermal (curves 1–4) and dynamic (curve 5).

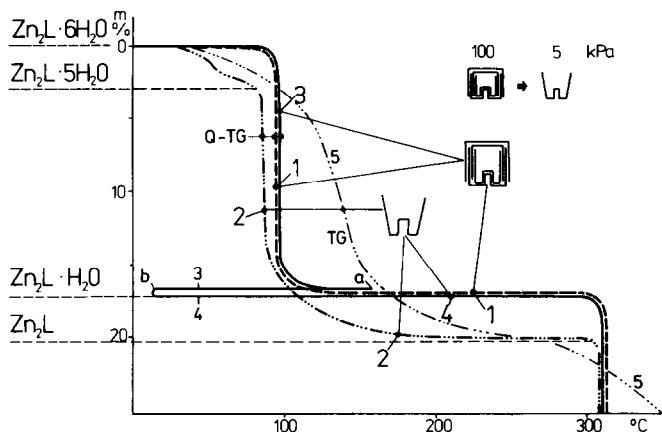


Fig. 27. Dehydration of Zn_2-EDTA chelate [25]. Sample holders: labyrinth (curves 1, 3) and open (curves 2, 4, 5) crucibles. Heating: quasi-isothermal (curves 1–4) and dynamic (curve 5). Heating interrupted in point *a*, cooled down, labyrinth crucible opened and heating started again at point *b*.

In connection with the change of reaction mechanism a particular memory effect (Table 5c) was also observed. The Q-TG curves in Fig. 27 illustrate the course of the dehydration of six water molecule containing ZnEDTA chelate [4,25]. As Fig. 27 proves, the decomposition took place in a different way in the labyrinth (curve 1) and open crucibles (curve 2). In the former case first pentahydrate was formed transitionally and the material was free from water at $150^\circ C$. In the latter case the chelate first lost five moles of water, and monohydrate was formed which decomposed at only $310^\circ C$. Thereafter the question was examined of how the monohydrate, formed in pure water vapour atmosphere, would behave if the partial pressure changed during the transformation. The monohydrate of the chelate was prepared by repeating the experiment using the labyrinth crucible in such a way that at $200^\circ C$ (point *a* of curve 3) the heating was interrupted and the sample suddenly cooled down. Thereafter at point *b* the crucible was opened and heating was started anew. As a result curve 4 was obtained. It can be seen that this curve runs parallel to curve 1 obtained not with the open (curve 2) but with the labyrinth crucible. This compound quasi-remembered its method of preparation. In other words, this means that only under the conditions ensured by the labyrinth crucible can monohydrate be formed. However, once this monohydrate is prepared, it will be stable up to $300^\circ C$ under the conditions offered by the open crucible as well.

Salt hydrates generally melt in their own crystal water in a congruent or incongruent way. The appearance of the liquid phase often directs the dehydration process to a new path [23,30,31,43] (Table 6a). If the decomposition pressure of the sample reaches a sufficiently high value before its melting point and the experiment is performed in an open sample holder,

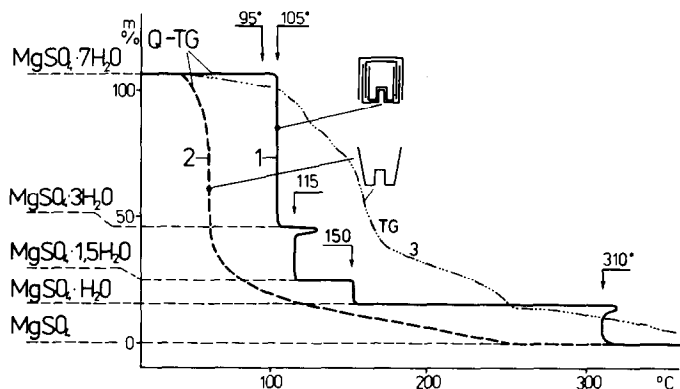


Fig. 28. Dehydration of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ [30]. Sample holders: labyrinth (curve 1) and open (curves 2, 3) crucibles. Heating: quasi-isothermal (curves 1, 2) and dynamic (curve 3).

then during the course of transformation the liquid phase would not be formed at all (curve 4 in Fig. 29) and water could depart in the form of water vapour directly from the solid sample, before its melting [30,35,41]. However, in the labyrinth crucible the liquid phase certainly appears, and this may cause the formation of new intermediates. This was observed [30] in the case of the decomposition of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Curve 2 in Fig. 28, recorded by using the open sample holder, shows that the sample lost, at 50°C , before melting (95°C), the greater part of its crystal water content. No sign can be found in the curve indicating the eventual formation of intermediates. In contrast to this, curve 1 traced by using the labyrinth crucible, proves the formation of three intermediates.

The labyrinth crucible creates normalized conditions even for processes taking place in the liquid phase. Within this crucible a pure water vapour atmosphere is being formed which keeps in equilibrium with the liquid phase, so the water vapour can escape only at the boiling point of the liquid (Fig. 16). Under such conditions the boiling point and composition of the liquid will change in a different way in the case of saturated and unsaturated solutions.

In curve 1 of Fig. 29, which demonstrates the water loss process of the solution which was formed after the congruent melting of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in the labyrinth crucible, both cases are represented together [4,35,36]. It is to be noted that sections *a-d* and *e-f* in curves 2 and 3 are not characteristic. The former could perhaps be described as an evaporation while latter as a drying process (Fig. 31).

The example also serves as a demonstration of further possibilities. In phase diagrams of water-salt systems the curve illustrating changes in the boiling point is often missing. Determination of the boiling point of concentrated viscous solutions is a rather difficult task. However, the determina-

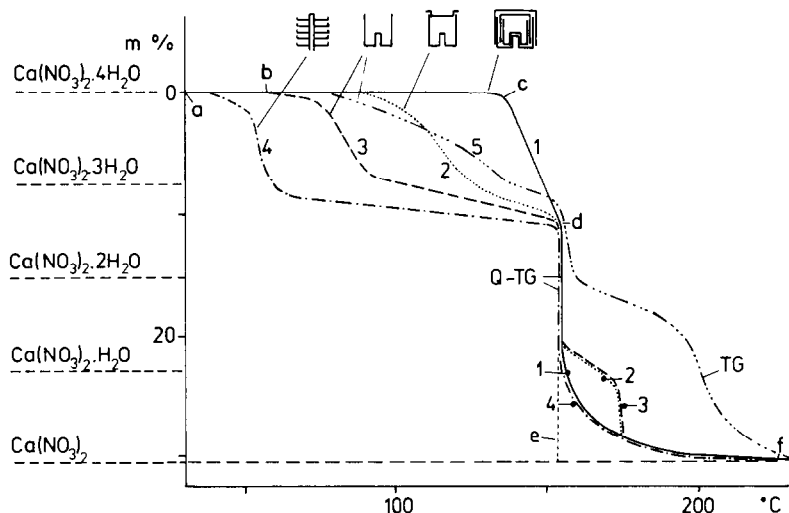


Fig. 29. Dehydration of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ [35,36]. Sample holders: labyrinth (curve 1), covered (curve 2) and open (curves 3, 5) crucibles and multiplate sample holder (curve 4). Heating: quasi-isothermal (curves 1–4) and dynamic (curve 5). Points *a–f*, see Fig. 30.

tion is rapid and accurate if the salt hydrate or its solution is placed in a labyrinth crucible and examined by the Q-TG technique. Projecting the related pairs of temperature–composition values of the Q-TG curve upon the phase diagram according to the principle illustrated in Fig. 30, the boiling phase curve (curve *c–d*) can easily be constructed. This figure shows the results of the examination of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (curves 1 and 3) and its solution containing 10% of $\text{Ca}(\text{NO}_3)_2$ (curves 2–4). Points *a–e* in curves 1 and 3 can be interpreted as follows. At point *a* the heating begins. At point *b* the salt hydrate congruently melts and a saturated solution is formed. Between points *b* and *c*, due to increasing temperature, the solution becomes more and more unsaturated. Departure of water vapour from the labyrinth crucible can only begin when the solution starts to boil at point *c*. Between points *e* and *d* the solution continuously becomes more concentrated while its boiling point increases. At point *d* the solution becomes saturated. Thereafter between points *d* and *e* solid $\text{Ca}(\text{NO}_3)_2$ separates while the temperature remains constant. Between points *d* and *e* the three, solid liquid and gas, phases remain in equilibrium. In the case of curves 2 and 4, due to the lower concentration, the boiling point (*c'*) is lower.

In the case of solutions formed at the melting of salt hydrates towards the end of the water loss process a solid crust readily forms [26,29,31,34–37,41] on the pulp-like surface of the mixture, consisting of the viscous solution and the solid crystals separated from it. Through this crust the water vapour from the inside of the sample can depart only with difficulty and therefore this process always drastically changes the course of conventional thermo-

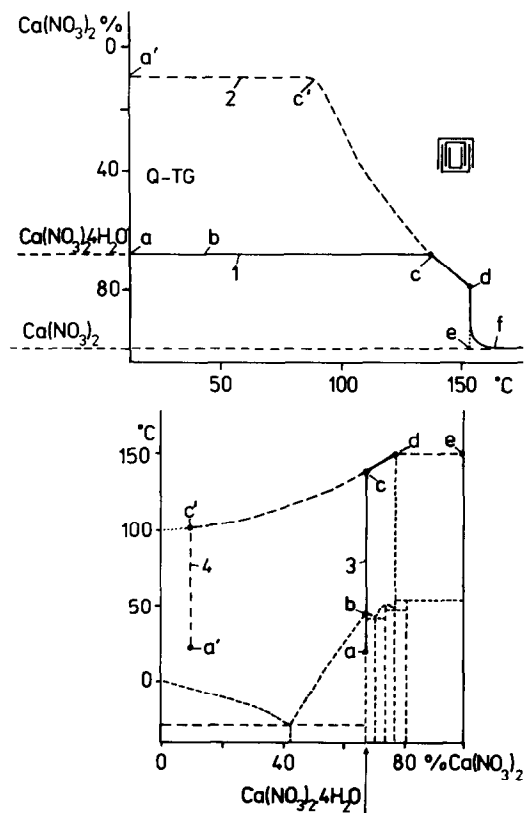


Fig. 30. Correlation between Q-TG curves and phase diagram of $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$ [35,36]. Q-TG curve of solid $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (curve 1) and its projected curve onto the phase diagram (curve 3). Q-TG curve of 10% $\text{Ca(NO}_3)_2$ solution (curve 2) and its projected curve onto the phase diagram (curve 4). Points: *a* (*a'*), examination starts; *b*, $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$ melts; *c*, boiling of the unsaturated solution starts; *d*, boiling of the saturated solution starts; *f* (theoretical *e*), end of water loss. Sample holder: labyrinth crucible. Heating: quasi-isothermal.

analytical curves. However, since its effect varies from case to case, the process can seldom be identified with certainty.

$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ was examined [31] and as Fig. 31 shows, it was found that the course of the Q-TG curves was regular with both the labyrinth (curve 1) and simple covered crucibles (curve 2). However, by using an open crucible (curve 3) or the multiplate sample holder (curve 4) it was observed that water loss took place stepwise and with great delay. The difference in the shape of the four curves can be explained only with crust formation. In general, by applying labyrinth and covered crucibles, there was no crust formation.

Exothermic reactions [4,44,45] take place spontaneously and if the conditions are favourable to the accumulation of liberated heat, then the reaction

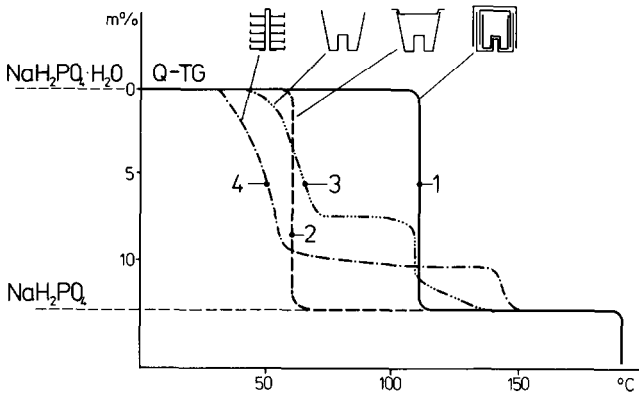


Fig. 31. Dehydration of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ [31]. Sample holders: labyrinth (curve 1), covered (curve 2) and open (curve 3) crucibles and multiplate sample holder (curve 4). Heating: quasi-isothermal (curves 1–4).

may even occur with an explosive rapidity. The quasi-isothermal heating controller system is also suitable for regulating such reactions. Figure 32 shows the decomposition process of nitrocellulose in N_2 atmosphere.

Curves 1, 3 and 6 were obtained under dynamic heating conditions while curves 2, 4 and 5 were traced under quasi-isothermal heating conditions. The substance was placed on the plates of the multiplate sample holder in the

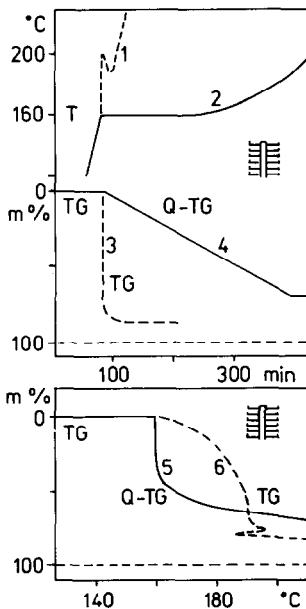


Fig. 32. Decomposition of nitrocellulose [27,45]. Sample holder: multiplate. Heating: quasi-isothermal (curves 2, 4, 5) and dynamic (curves 1, 3, 6).

form of a solution. After drying a thin film of nitrocellulose was formed. When the temperature was increased at a rate of $3^{\circ}\text{C min}^{-1}$, the material decomposed at explosive speed (curve 3) while the temperature of the sample suddenly increased by 35°C (curve 1). In contrast, by applying the quasi-isothermal heating technique the decomposition of nitrocellulose could be slowed down in such a way (curve 4) that the decomposition took place very slowly (0.5 mg min^{-1}) and at a constant rate. This was possible because the heat-controlling system kept the temperature of the furnace lower than that of the sample during the whole transformation and established the necessary difference between the sample and furnace temperatures.

Enthalpy changes, accompanying thermal transformations, can be seen in another light if, beside the Q-TG curve, Q-DTG and Q-DTA curves are simultaneously traced. Figure 33 shows the original picture of the first two dehydration processes of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, obtained by means of the new type of Derivatograph working with a microprocessor [15] and using the labyrinth crucible. A difference is seen in the course of the Q-DTG and Q-DTA curves which may be explained in the following way. The salt hydrate melted between 92 and 100°C and solid $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ and a saturated solution phase form. This process is demonstrated by the 97°C peak in the Q-DTA curve. Departure of the first two water molecules from the labyrinth crucible could only start after the saturated solution began to boil. As is well known, these two processes do not separate in conventional DTA curves. From the Q-DTA curve it is remarkably clear that the first step of the weight change is connected with a smaller enthalpy change than the second one. Assuming that using the quasi-isothermal measuring technique stan-

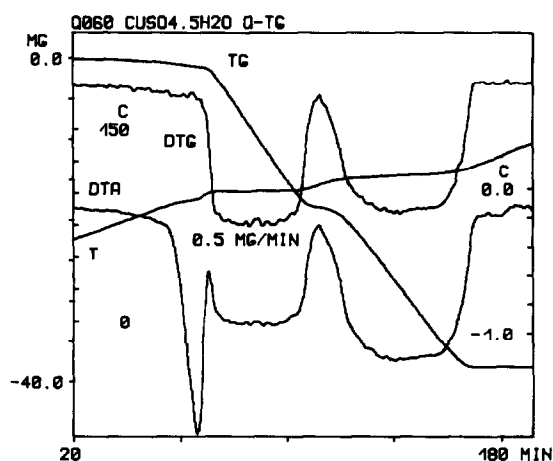


Fig. 33. Dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ examined by means of Derivatograph-C [15] (original thermogram). Sample holder: labyrinth. Heating: quasi-isothermal, heating control by Q-DTG signal, decomposition rate: $dm/dt = 0.5 \text{ mg min}^{-1}$, $\Delta m = 100 \text{ mg}$.

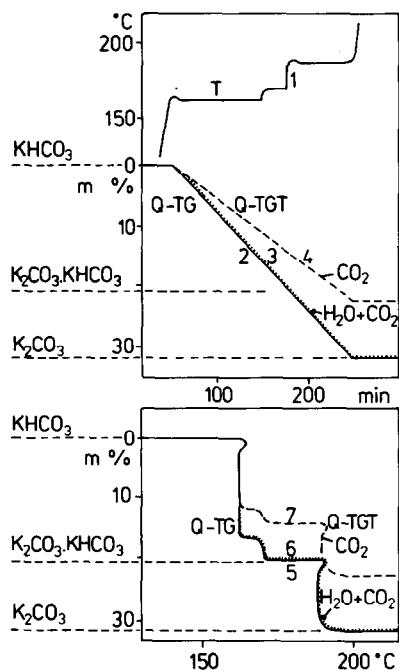
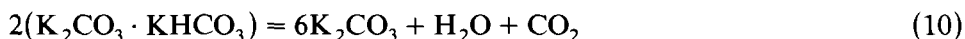
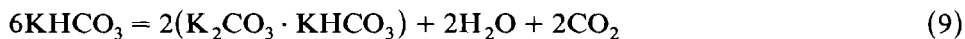


Fig. 34. Decomposition of KHCO_3 examined by the simultaneous Q-TG and Q-TGT technique [11]. Sample holder: labyrinth. Heating: quasi-isothermal, heating control by Q-DTG signal, decomposition rate: dm/dt 0.5 mg min^{-1} , $\Delta m = 100 \text{ mg}$.

Standard conditions can be ensured, it follows that after calibrating the apparatus, the transformation heat can be determined with a greater accuracy than by means of conventional DTA devices.

By combining the Q-TG measuring technique with the method of thermogas-titrimetry good results can also be obtained in the analysis of reaction mechanisms [18,20,21,28,43–45]. The decomposition of KHCO_3 is known in the literature as a one-step process (curve 4 in Fig. 3). In the course of the examination under quasi-isothermal–quasi-isobaric conditions, it turned out that the decomposition took place gradually [5c]. From the break dividing the Q-TG curve (curve 5 in Fig. 34) into two parts of proportions 2:1, one could suppose that the reaction took place either according to eqns. (7) and (8) or (9) and (10)



Solely on the basis of the Q-TG curve it was not possible to decide on which of the two paths the transformation took place. So, the experiment

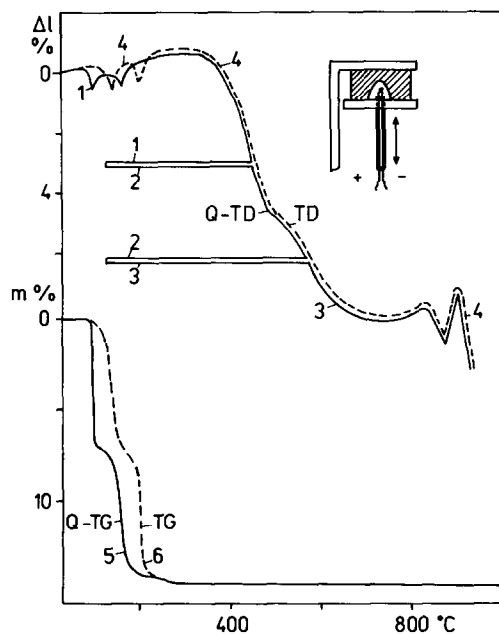


Fig. 35. Dehydration and recrystallization of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ examined by TD and Q-TD techniques [27,48]. Heating: quasi-isothermal (curves 1, 2, 3, 5), rate of the process, $dI/dt = 0.03 \text{ mm min}^{-1}$, $\Delta l = 3 \text{ mm}$, heating controlled by Q-DTD signal and dynamic (curves 4, 6), heating rate: 5°C min^{-1} . Length of the pressed test piece, $l = 30 \text{ mm}$.

was repeated so that the Q-TGT curve was simultaneously recorded with the Q-TG curve [11] and it turned out that reactions (9) and (10), respectively, must have taken place. Curves 3 and 6, which were obtained from Q-TGT 4 and 7 by recalculation with the equivalent $\text{CO}_2 + \text{H}_2\text{O}$, can be brought into superposition with Q-TG curves 2 and 5, respectively (Fig. 34).

Thermal reactions of solid compounds are accompanied by inner structural transformations. These can successfully be examined by the method of dilatometry. Quasi-isothermal dilatometry (Fig. 35) allows the study of such structural transformations according to new points of view [4,12] as can be seen from the following example.

It is known that $\text{BaCl} \cdot 2\text{H}_2\text{O}$ loses its water of crystallization up to 300°C and the residue is amorphous BaCl_2 . The water loss, leading to equilibrium, as well as the connected change in size of the pressed test piece, were indicated in the TD, TG (curves 4 and 6), Q-TD and Q-TG curves (curves 1 and 5) by a significant shift in phase. However, between 300 and 800°C the test piece contracted in the case of both kinds of examination to the same extent (about 8%) and any shift in the phase could be observed between the TD and Q-TD curves. Furthermore, when the Q-TD examination was interrupted and then restarted, the process continued from the very point where it was interrupted. Accordingly, in the recrystallization process no

change occurred due to the drastic reduction in heating rate. It seems that every phase of the recrystallization process depended solely on the actual temperature value related to it.

Summing up, it can be stated that in the formation of conventional thermoanalytical curves, heat and gas transport processes really play a defining role. However, as it was shown, beside these, many other factors may also influence the shape of the curves, such as the effect of gaseous products, of foreign gases and of solid surfacial contaminants, exerted upon the active sites or crystals and upon nucleus formation and nucleus growth, respectively, the porosity of the new phase, lattice stress caused by foreign ions and dislocations, the lasting presence or rapid disappearance of minute amounts of a solution phase, crust-formation or the lack of it on the surface of salt hydrates in contact with their saturated solution, etc. These are all factors independent of the essence of the reaction, but which may significantly influence the performance of the reaction itself.

Based on these findings, the authors regard their earlier statement to be completely justified, that "the correctness of reaction kinetic calculation on the basis of curves obtained by dynamic thermoanalytical methods is rather questionable" [5c].

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