TRANSFORMATION-GOVERNED HEATING TECHNIQUES IN THERMAL ANALYSIS I.

F. Paulik

Institute for General and Analytical Chemistry, Technical University Budapest
Budapest, 1521 Hungary

Abstract

The author gives a detailed survey on thermogravimetric investigations under quasi-isothermal – quasi-isobaric conditions (Q-TG). According to the principle of the technique the heating of the sample is governed by the transformation itself according to the feed-back principle in a way that the transformations should take place at a strictly constant rate, slower by orders of magnitude than in the case of the conventional techniques. Due to this, the transformations take place under ideal conditions, near to physico-chemical requirements.

Based on the obtained advantageous results further methods were elaborated, like thermo-dilatometry (Q-TD), evolved gas analysis (Q-EGA) and microdistillation under quasi-isothermal conditions.

The second part of the present review deals with DTA and DSC techniques under quasi-isothermal conditions elaborated recently.

Keywords: dilatometry, evolved gas analysis, microdistillation, thermogravimetry

Introduction

Physical chemists often give voice to criticism in the sense that the non-isothermal thermal analytical methods do not reflect the real nature of transformation. This criticism is well-grounded.

It is known that under the conditions for non-isothermal thermal analytical investigations, the course of heterogeneous reactions leading to equilibrium is basically governed by heat- and gas-transport processes, whereas that of reactions not leading to equilibrium by heat-transport only, which processes are out of our interest [1, 2]. This harmful effect is further modified by eventual changes in the experimental conditions. This is why the course of thermal analytical curves is often more characteristic of heat- and gas-transport processes than of the transformation itself [3, 4].

Moreover, the transformations are combinations of numerous elementary physical and chemical processes [2]. In fact, the aim of our investigation would be to detect and study these processes, but due to the strong deteriorating effect, they cannot be reflected in the course of the curves, thus they remain hidden to us.

During the development of this method, numerous attempts have been made to eliminate this drawback (measurements in low pressure and high pressure atmospheres, or in self-generated atmosphere, the development and use of micro-techniques, as well as the method of step-wise isothermal heating, etc.). However, both the setting of objectives and the set of tools were strongly restricted, thus the results achieved remained also poor. The first purposeful experiment for the elimination of this problem was carried out in 1962 by the elaboration of the quasi-isothermal, quasi-isobar thermal gravimetry [1–4, 5a–5d].

Table 1 Quasi-static measuring techniques

	Authors	Patent applied, paper appeared	Ref.	Heating control by the signal	Measured variables
I	L. Erdey, F. Paulik, J. Paulik F. Paulik, J. Paulik, L. Erdey F. Paulik, J. Paulik F. Paulik, J. Paulik	1962 1963 1971 1972	5.a 5.b 5.c 5.d	dm/dt	Q-TG
II	J. Rouquerol	1964	6	dp/dt	T
III	C. M. Bean, R. H. Oliver	1964	7	T	T
IV	J. Rouquerol	1969	8	dp/dt	TG
V	F. Paulik, J. Paulik	1973	3	dm/dt	Q-TG, Q-DTA
VI	F. Paulik, J. Paulik	1973	9	dm/dt	Q-TG, Q-EGA
VII	J. Paulik, F. Paulik	1973	10	dl/dt	Q-TD
VIII	O. T. Sørensen	1978	11	$T_1, T_2, ...T_n$	TG
IX	O. T. Sørensen	1980	12	$T_1, T_2, ...T_n$	TD
X	J. Paulik, F. Paulik, M. Arnold F. Paulik	1985 1995	13 2	dT/dt	T′
XI	F. Paulik, S. Gál, K. Mészáros-Szécsényi	1994	14	dm/dt	Q-TG′
XII	F. Paulik, E. Bessenyey-Paulik, K. Walther-Paulik	1997	15	dT/dt	Q-TA$_T$

Subsequently, several methods have been elaborated [4] with the same objective, but by using different techniques (Table 1). Thus, e.g. Rouquerol [6] published a method in 1964, in which the temperature-changes in the sample during reaction could be followed. In this case, the heating of the furnace was governed by the rate change in the liberation of the gaseous decomposition product. This method of heating regulation, which is called 'constant rate-controlled thermal analysis', in short, CRTA method, was suggested by the author in 1969 also for the study of the mass change in the sample [8].

Recommendation for a unified nomenclature

The names of methods proposed by authors and summarized in Table 1 are used in the literature inconsequently and not in a concise way. In order to solve this discrepancy, it would be advisable to accept a common designation of these methods, as e.g. 'quasi-static' thermal analysis, independently of the various authors and methods, respectively, as it was already suggested earlier [4]. In this case, each author can use his own designation, e.g. 'constant rate-controlled thermal analysis' [8], 'stepwise isothermal thermal analysis' [11], or 'quasi-isothermal thermal analysis' [5], which is characteristic of the principle of the method.

Quasi-isothermal, quasi-isobar thermogravimetry (Q-TG)

Paulik, Paulik and Erdey built their apparatus in 1962. The fundamental principle was patented in Hungary [5a] and in six further countries [5b]. This heating technique [5c] was later developed by applying a special kind of sample holder, the so-called labyrinth crucible [16], which ensured that transformation should take place in a self-generated atmosphere [5d]. The measuring system (Derivatograph C) was manufactured by the Hungarian Optical Works, (MOM) Budapest.

Operation principle of quasi-isothermal heating control [1–5]

The temperature of the sample is elevated by the heating control system of the simultaneous TG, DTG, DTA apparatus (Derivatograph) [1, 2] in the traditional way with a uniform rate, while the mass of the sample remains constant. However, when the mass of the sample begins to change, and the signal of the rate of mass change (DTG) achieves a predetermined value, a limit value sensor switch starts to operate. This switch sends a command to the heating control, not to increase further or even decrease the temperature of the furnace, and with this, also the rate of mass change. When this latter falls below a predetermined value, the heating control increases the intensity of heating again. This cycle, which lasts only for seconds, is repeated in a great number up to the end of the transformation.

In order words, on the basis of 'feed-back', the transformation itself regulates the heating in such a way that between the temperatures of the sample and the furnace a constant and automatically generated difference exists so that the change in the mass of the sample takes place with a very small and constant rate, which is orders of magnitudes smaller than the traditional rate.

According to experience, by applying this method of heating, there is enough time for the sample to take up or give down heat without any delay from or to its environment, without any temperature drop in the internal part of the sample, that may be considered as one source of deterioration.

After the reaction is ended, the heating regulation system again raises the temperature of the furnace in a quick, non-isothermal way, until the start of the next transformation.

*Labyrinth sample-holder – 'self-generated' atmosphere*

It can be proved that by applying the traditional, non-isothermal heating mode, the partial pressure of the gaseous decomposition products in the internal part of open sample-holders changes continuously and in an unforeseeable manner. Consequently, the characteristic temperature of transformations changes in a not interpretable way, as well [2].

In order to get rid of this discrepancy, the so-called 'labyrinth sample-holder' has been constructed [1–4, 16, 17]. In this labyrinth crucible (Fig. 1), namely, a practically 100% pure 'self-generated' atmosphere develops immediately after the beginning of the decomposition, the composition of which atmosphere does not change till the end of the transformation, thus a quasi-isobar condition can be realised.

However, the discrepancy in non-isothermal cases can be only partially eliminated this way, as demonstrated by the course of curve 8 in Fig. 1. This curve is taken by using the labyrinth crucible, but still with the non-isothermal heating mode. Though in this case decomposition took place not in a broad temperature interval of several hundred degree centigrades, but the interval was still between 900 and 1000°C. This can be explained by the fact that the sample was unable to take up the transformation heat momentarily from its environment, heat-transport was drawn off in time, and in the meantime, the non-isothermal heating program raised further the temperature of the sample without any reason.

According to curve 4 in Fig. 1, correct results could be obtained, when the labyrinth crucible and the quasi-isothermal heating program were used simultaneously.

For example, according to curve 4 in Fig. 1, the decomposition of calcium carbonate occurs isothermally, at 893±2°C, which value agrees quite well with the data
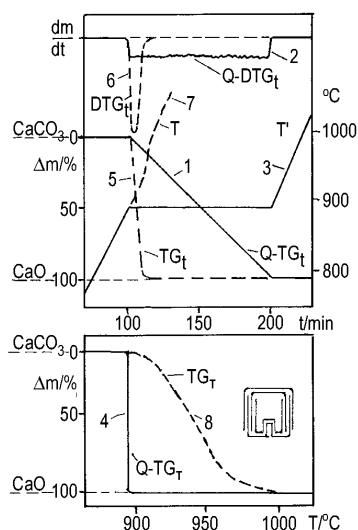
Fig. 1 Decomposition of $CaCO_3$ under quasi-isothermal, quasi-isobaric (curves 1–4) and conventional (curves 5–8) conditions, using labyrinth crucible

of $895\pm1^{\circ}C$ known from literature and calculated from caloric data by thermodynamical calculations.

From all this it can be concluded that the decomposition of calcium carbonate takes place not only quasi-isothermally and under quasi-isobar conditions, but, if not in the strict sense, it occurs also near to equilibrium, approximately under quasi-equilibrium conditions, which fact presumedly already approaches the requirements of physical chemists.

A further practical advantage is that by this measuring technique the so-called normal transformation temperature belonging to the 100 kPa partial pressure of its gaseous decomposition products can be determined with an approximate accuracy for any unknown reaction leading to equilibrium or for its any elementary step.

Interpretation of curves

Curves 1–4 in Fig. 1 have been taken by the quasi-isothermal heating technique, whereas curves 5–8 by using the labyrinth crucible, but applying traditional, non-isothermal heating.

As it is seen from the course of the Q-TG$_t$ and Q-DTG$_t$ curves, these curves provide quite a few information. From the Q-TG$_t$ curve in Fig. 1, no conclusion can be drawn concerning the course of the transformation, at best something can be said on mass change. Curve 2 in Fig. 1, i.e. the Q-DTG$_t$ curve, can serve for checking the correct operation of the apparatus.

In fact, information is carried by curve 3, the temperature curve in Fig. 1. The heating program influences directly the temperature of the sample only in the non-isothermal heating period. During transformation, in the so-called quasi-isothermal heating period, the Q-DTG$_t$ signal (curve 2), that means, the transformation itself takes over the control of temperature from the heating programmer by a feedback mechanism. Thus, in this period, the course of the temperature curve is characteristic of the elementary steps governing transformation.

About the stoichiometry of the transformation containing already quantitative data as well, information can be obtained from the Q-TG$_T$ curve, which corresponds to the earlier Q-TG$_t$ curve only taken as the function of sample temperature (T'). It is usual to publish the results of thermal analytical investigations in this form.

The course of T' and Q-TG$_T$ curves changes depending on the nature of the transformation, on its being equilibrium or non-equilibrium nature.

Course of T' and Q-TG$_T$ curves in transformations leading to equilibrium

From the nature of reactions leading to equilibrium it follows that the course of the reaction depends on the partial pressure of the gaseous decomposition product being in contact with the sample.

As we have seen, in the case of a labyrinth crucible a pure, self-generated atmosphere of atmospheric pressure and its constancy is ensured, thus the section in question of the T' and Q-TG$_T$ curves show an isothermal course (Fig. 1, curves 3 and 4).

However, the course of the reaction is also isothermal (Fig. 2), if a less closed sample holder is applied (covered or uncovered crucible, multiplate sample holders) but, due to the more or less intense ventilation, the partial pressure of the gaseous decomposition product remains below 100 kPa. Namely, the heating control automatically ensures the constancy of the rate of transformation and through this, that of the liberation of gaseous decomposition product. Thus, at the beginning of the transformation, in the environment of the sample a gas composition corresponding to ventilation conditions in the sample holder develops, and this composition remains constant up to the end of reaction.

Thus, reactions leading to equilibrium have two distinctive features:

a) The Q-TG$_T$ curve is of an isothermal course

b) The temperature of decomposition works out correspondingly to the partial pressure of the gaseous decomposition product, but it remains constant during the transformation.
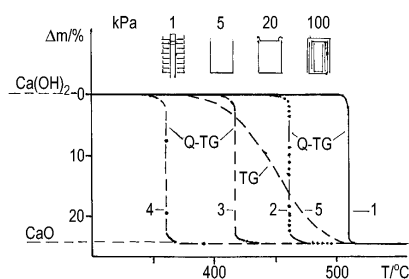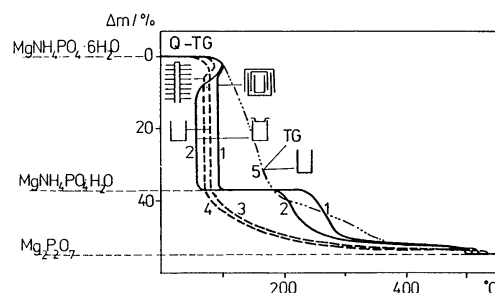

Fig. 2 Dehydration of Ca(OH)$_2$ under quasi-isothermal, quasi-isobaric (curves 1–4) and conventional (curve 5) conditions, using different kind of sample holders

As these criteria are fulfilled in curves 1–4 in Fig. 2, we can establish that the dehydration of calcium hydroxide is a process leading to equilibrium.

By knowing the equilibrium decomposition pressure–temperature correlation and the actual partial pressure of the gaseous decomposition product or its decomposition temperature, from the known data the unknown quantity can be calculated [1, 2]. For example, in the case of calcium carbonate decomposition, with such a calculation, for the actual partial pressures in labyrinth, covered, uncovered and multiplate sample holders, following partial pressure values have been obtained by a rough approximation, respectively: 100, 20, 5 and 1 kPa [1]. It is right to suppose that the composition of the gas atmosphere in connection with the sample is similar also for other gaseous decomposition products.
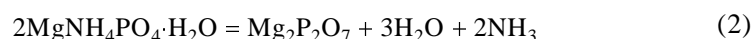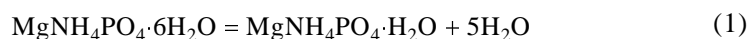
Changing the sample holder types is a useful tool for directing the elementary steps of complex chemical reactions into another direction without the need of decreasing the pressure, thus for obtaining further useful information on the mechanism of transformations [1].

For example, in Fig. 3, a strange phenomenon can be observed [2, 17]. The decomposition of magnesium-ammonium phosphate hexahydrate in uncovered and

Fig. 3 Decomposition of $MgNH_4PO_4 \cdot 6H_2O$ under quasi-isothermal, quasi-isobaric (curves 1–4) and conventional (curve 5) conditions, using different kind of sample holders

multi-plate sample holders took place at lower temperatures than in the labyrinth crucible, but at a higher temperature than in the covered sample holder. The explanation for this is that at higher vapour contents (curves 1 and 2), decomposition occurred stepwise.

$$MgNH_4PO_4 \cdot 6H_2O = MgNH_4PO_4 \cdot H_2O + 5H_2O \qquad (1)$$

$$2MgNH_4PO_4 \cdot H_2O = Mg_2P_2O_7 + 3H_2O + 2NH_3 \qquad (2)$$

whereas at lower water vapour partial pressures the decomposition takes place in one step:

$$2MgNH_4PO_4 \cdot 6H_2O = Mg_2P_2O_7 + 13H_2O + 2NH_3 \qquad (3)$$
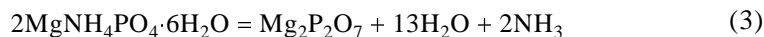
The anomalous (irregular) sequence in the first sections of the four curves has two reasons. The first one is that the equilibria for the two kinds of reactions (1 and 3 resp.) followed different decomposition pressure–temperature correlations, and the other one is that for every curve pairs the difference in the partial pressure of decomposition products further modified the decomposition temperature.

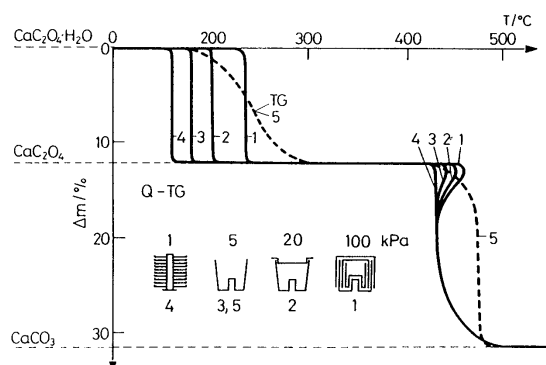### Course of T' and Q-TG_T curves in reactions not leading to equilibrium

By using the quasi-isothermal heating technique, the course of reactions not leading to equilibrium can be characterized by the following criteria:

a) The course of T' and Q-TG_T curves is independent of the concentration (partial pressure) of decomposition products

b) The T' temperature of the sample varies during transformation in a special way, thus the course of the Q-TG_T curve is not isothermal.

This latter statement needs some more explanation. The driving force in this transformation is also the heat up-take of the sample, but its intensity is influenced by different elementary processes, such as nucleus formation, nucleus growth, diffusion of gaseous decomposition products through the new phase depending on its po-

rosity, the reaction-inhibiting or -stimulating effect of gas molecules adhering to the active sites of crystals, diffusion in the solid phase, and last but not least, the nature of the reaction in question [2] i.e. its not leading to equilibrium (e.g. decomposition of CaC_2O_4).

The fundamental principle of quasi-isothermal measuring technique commands that transformations should take place with a low and strictly constant rate. The heating program regulates the sample temperature at the command of the $Q\text{-}DTG_t$ signal correspondingly to the above prescription. As the decomposition mechanism of reactions not leading to equilibrium, as well as the majority of the above listed elementary processes have a decreasing effect on the reaction rate, the heating control modifies the temperature of the sample continuously by the feedback principle so that the above condition should be fulfilled. This modification is, in the majority of cases, a temperature increase. Of course, if it becomes necessary, the control can also decrease the sample temperature and with it, the rate of reaction.

Fig. 4 Decomposition of $CaC_2O_4 \cdot H_2O$ under quasi-isothermal, quasi-isobaric (curves 1–4) and conventional (curve 5) conditions, using different kind of sample holders

Thus, the course of T' and $Q\text{-}TG_T$ curves indirectly carries important and characteristic information on the nature of reactions and different elementary processes.

Figure 4, depicting the course of the decomposition of $CaC_2O_4 \cdot H_2O$ in a nitrogen atmosphere, is very instructive. From the isothermal course of the first section of curves 1–4, and from the fact that they depend on the partial pressure of the gas-eous decomposition product it follows unambiguously that the loss of crystal water is a reversible process leading to equilibrium. To the contrary, the course of the four curve sections in the second step are identical and of non-isothermal character, thus it can be established that the decomposition of the dehydrated, water-free calcium oxalate is an irreversible reaction not leading to equilibrium. In the knowledge of the mechanism of the decomposition, this feature is beyond all question.

By analysing the non-isothermal section of the $Q\text{-}TG_T$ curve it can also be established that decomposition is introduced by nucleus formation. This can be the explanation for the beak-shaped first section of the curve. The sample has been temporar-

ily overheated, but when enough nuclei have already been present, the sample temperature has spontaneously returned to its original decomposition temperature.

But how was the nucleus formation influenced by the change of sample holders? The most probable explanation for this is that in the case of labyrinth crucible, i.e. when a pure water vapour atmosphere was present, compact solid intermediates having less active sites for nucleus formation have been formed, in contrast to the more open sample holders, where products of higher porosity could be developed.

*Complex transformations consisting of several elementary processes*

The decomposition of CaC_2O_4 is not the only reaction in which the gaseous decomposition product exerts a secondary effect on the reaction by inhibiting or initiating it, or even by directing it into another direction. Such an example is e.g. the decomposition of $CoNH_4PO_4 \cdot H_2O$ in a nitrogen atmosphere, the course of which process is shown in Fig. 5 [18].
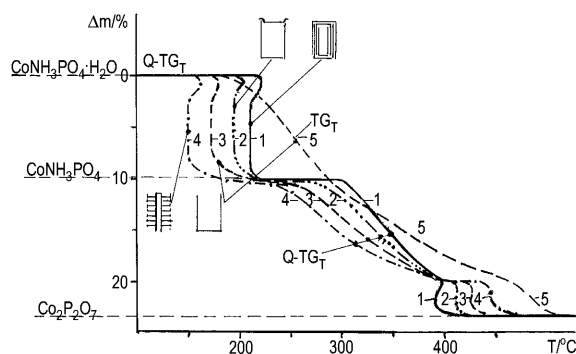
Fig. 5 Decomposition of $CoNH_4PO_4 \cdot H_2O$ under quasi-isothermal, quasi-isobaric (curves 1–4) and conventional (curve 5) conditions, using different kind of sample holders

The isothermal course of the first sections in curves 1–4, together with their regular sequence proves that the loss of crystal water leads to equilibrium. After this, the intermediate $CoNH_4PO_4$ loses its ammonia content and structural water simultaneously. This process leads, by all probability, also to equilibrium. However, the strongly non-isothermal character of the curve can be attributed to the bulk, solid structure of the newly formed phase. By the progress of the transformation, diffusion through the ever thickening crust of the new phase becomes more and more difficult. This is why transformation could proceed only sluggishly in the temperature interval around 200°C. This hypothesis of the formation of a solid crust is supported also by the fact that the curves formed a node around 380°C, and their sequence also turns round. This can only be imagined, if the crust becomes more porous in the ammonia and water vapour-rich atmosphere i.e. in labyrinth crucible.

In the Q-TG_T curve of Fig. 6 illustrating the dehydration process of hydrargillite, the phenomenon of competition of two reactions occurring rarely in thermal reac-
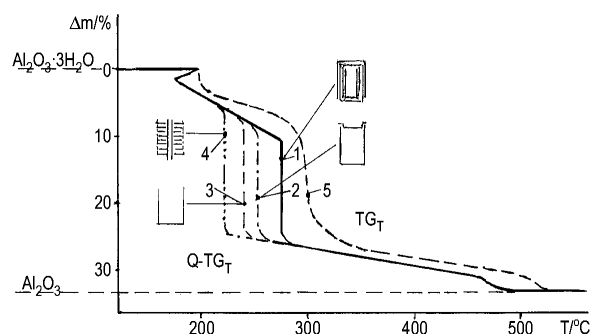
Fig. 6 Decomposition of gibbsite under quasi-isothermal, quasi-isobaric (curves 1–4) and conventional (curve 5) conditions, using different kind of sample holders

tions, can be studied [19]. The decomposition of hydrargillite is also introduced by a strongly delayed nucleus formation proven by the beak-shaped section at the start of the curve. In the course of decomposition, first boehmite is formed:

$$2\alpha-Al(OH)_3 \rightarrow 2\alpha-AlOOH + 2H_2O$$
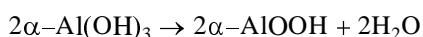
According to the course of the curve, this process did not lead to equilibrium, as the transformation was non-isothermal.

In the case of the labyrinth crucible, the Q-TG$_T$ curve suddenly changed direction at 270°C, at which point an isothermal transformation started. Hydrargillite still not decomposed, decomposed directly to Al_2O_3 and H_2O without any change in temperature at this point.

$$2\alpha-Al(OH)_3 \rightleftarrows \chi-Al_2O_3 + 3H_2O$$
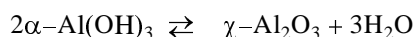
When the decomposition of hydrargillite started, formation of boehmite immediately stopped, since to its continuation the temperature of the sample should have been increased due to its non-isothermal nature. However, the heating program did not perform this task, since decomposition of hydrargillite took place without raising the temperature as well, fulfilling the requirement of the measuring technique, namely that the mass of the sample should change with a small, predetermined and strictly constant rate.

α-AlOOH formed in the first phase of the transformation decomposed at around 470°C, according to the equation:

$$2\alpha-AlOOH \rightarrow \gamma-Al_2O_3 + H_2O$$
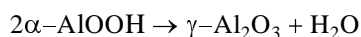
The phase diagram is a rich source of data for the equilibrium relations of multi-component systems, therefore it is a great assistance in the interpretation of thermal analytical curves, but only if transformations occur under near-equilibrium conditions. Figures 7.I and 7.II prove convincingly that curves taken by the quasi-isother-

mal measuring technique satisfactorily fulfil this requirement (curve 1), in contrast to curves taken by the traditional method (curve 2), which do not.

Curve 1 in Fig. 7.I shows the course of decomposition for $Ca(NO_3)_2 \cdot 4H_2O$ by the quasi-isothermal, quasi-isobar measuring technique, whereas curve 2 illustrates the same decomposition under traditional, non-isothermal conditions [2, 21]. The course of these curves can be interpreted by the aid of the phase diagram in Fig. 7.II:

Under the conditions of taking up curve 1, $Ca(NO_3)_2 \cdot 4H_2O$ is melted congruently (point b). The solution being saturated at the beginning, becomes unsaturated with increasing temperature (points b–c), but no water vapour leaves the labyrinth crucible till point c. The now unsaturated solution starts to boil at $135^\circ C$ (point c), it looses water gradually, while temperature increases gradually to $153^\circ C$ (point d). At this point, the solution becomes again saturated. Subsequently, it looses further amounts of water by boiling, in an isothermal way, while solid $Ca(NO_3)_2$ is precipitated in an amount proportional to the water loss. After point e, from the pulp remnant, which around $150^\circ C$ contained a viscous solution consisting of only half a molecular mass of water and of $Ca(NO_3)_2$ crystals, water vapour can diffuse out only with difficulty (curve section e–f).
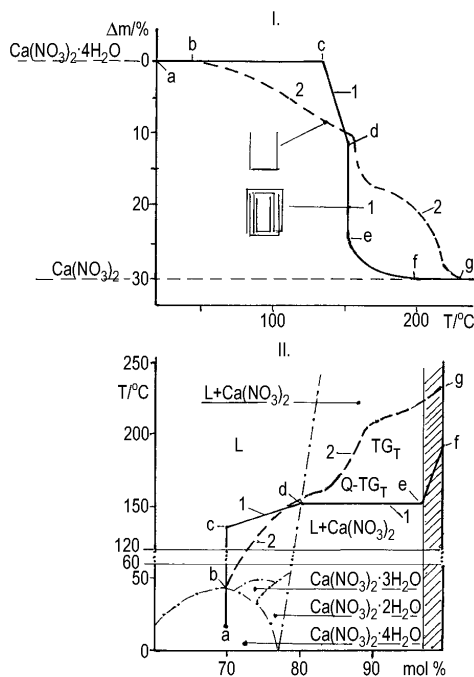
Fig. 7 I. Dehydration of $Ca(NO_3) \cdot 4H_2O$ under quasi-isothermal, quasi-isobaric (curve 1) and conventional (curve 2) conditions, using a labyrinth (curve 1) and an open (curve 2) crucible.

II. Phase diagram of $Ca(NO_3)_2$ and H_2O system containing the tracing of curves 1 and 2 from Fig. 7.I Curves 1 and 2 in Fig. 7.I and Fig. 7.II, despite their different shape illustrate the same process

Quasi-isothermal investigations are only apparently too time-consuming. Heating regulation operates, namely, only in the period of transformation by producing quasi-static conditions. In transformation-free sections the rate of non-isothermal heating remains unchanged, i.e. $5-10^{\circ}C$ min^{-1}. According to experience, the time requirement of a measurement is only doubled. However, for this time loss, more than compensates us the excess information obtained by taking the Q-TG$_T$ curves.

Simultaneous quasi-isothermal thermogravimetric (Q-TG) and thermal gas titrimetric (Q-TGT) study

From the course of the thermal gravimetric (TG) curve of a complex transformation consisting of several elementary reactions, only the resultant of the mass changes in the elementary reactions can be observed. By the thermal gas titrimetric study, however, the individual elementary reactions can selectively be determined, independently of each other. From the simultaneous, quasi-isothermal performance of the two studies, multiplied selectivity values and resolution is to be expected [1, 2, 9].

Thermal dilatation study under quasi-isothermal, quasi-isobar conditions (Q-TD)

Thermal decomposition, solid phase reactions of inorganic substances and minerals, as well as changes in the crystal structure and dispersity usually involve measurable changes in volume. This can be followed by thermal dilatation measurements. During the above listed transformations diffusion plays a key role, which is a slow, strongly temperature dependent process. It is easy to see that by realising quasi-static conditions by means of quasi-isothermal heating higher selectivity and better resolution can be achieved. The heating control of the dilatometer is governed in this case by the derivative (Q-DTD) of the thermal dilatation curve (Q-TD) [1, 2, 10].

Micro-distillation study of liquid mixtures by the thermal gravimetric method under quasi-isothermal, quasi-isobar conditions

Separation of the components of liquid mixtures by distillation is a difficult task owing to the interaction of the components (formation of azeotropic mixtures, etc.). Due to the slow rate of reaching equilibrium, time plays also here a very important role. According to experience [14], by thermal gravimetric measurements carried out under quasi-isothermal and quasi-isobar conditions it is possible to perform micro-distillation near to equilibrium. This method is a twin to the quasi-isothermal thermal gravimetric measuring technique. By this method, namely, instead of the gaseous decomposition products of solid materials, we measure mass decrease owing to leaving vapours from the boiling liquid mixtures due to distillation. Instead of the quick heating used in traditional distillations, in this case the regulation of tempera-

ture is taken over by the derived thermal gravimetric curve (Q-DTG), again on the basis of feed-back. The accuracy of this measurement is increased also by the fact that the liquid mixture to be studied is placed into a labyrinth crucible, thus the boiling liquid is in equilibrium with the 'self-generated atmosphere' of the leaving vapours [2, 14].

References

1   J. Paulik and F. Paulik, Simultaneous Thermoanalytical Examinations by Means of the Derivatograph, Elsevier, Amsterdam 1981.
2   F. Paulik, Special Trends in Thermal Analysis, Wiley, Chichester 1995.
3   F. Paulik and J. Paulik, J. Thermal Anal., 5 (1973) 253 (review).
4   F. Paulik and J. Paulik, Thermochim. Acta, 100 (1986) 23 (review).
5a L. Erdey, F. Paulik and J. Paulik, Hung. patent N^o: 152197 (1962).
5b F. Paulik, J. Paulik and L. Erdey, Patents of 5.a. in: USA, UK, Germany, France, Switzerland, Italy (1962).
5c F. Paulik and J. Paulik, Anal. Chim. Acta, 56 (1971) 328.
5d F. Paulik and J. Paulik, Anal. Chim. Acta, 60 (1972) 127.
6   J. Rouquerol, Bull. Soc. Chim. Fr., (1964) 31.
7   C. M. Bean and R. H. Oliver, Engl. patent N^o: 1063898 (1964).
8   J. Rouquerol, Thermal Analysis, Proc. 2nd ICTA Conference Worchester, Academic Press, New York 1969.
9   F. Paulik and J. Paulik, Anal. Chim. Acta, 67 (1973) 437.
10 J. Paulik and F. Paulik, Thermal Analysis, Proc. 5th ICTA Conference, Kyoto, Heyden and Sons, London 1977.
11 O. T. Sørensen, J. Thermal Anal., 13 (1978) 429.
12 O. T. Sørensen, Thermal Analysis, Proc. 6th ICTA Conference, Bayreuth, Birkhauser Verlag, Basel 1971.
13 J. Paulik, F. Paulik and M. Arnold, Hung. patent N° 193114 (1985) patents in: USA, UK. Germany, France, Switzerland, 1985.
14 F. Paulik, S. Gál and K. Mészáros-Szécsényi, J. Thermal Anal., 42 (1994) 425.
15 F. Paulik, E. Bessenyei-Paulik and K. Walther-Paulik, PCT (HU 98) 00041 patents applied in Europe, USA, Japan.
16 F. Paulik and J. Paulik, Hung. patent N^o: 163305 (1971) Patents in: USA, UK, Germany, France, Italy, Switzerland, Japan.
17 J. Paulik and F. Paulik, Proc. 4th ICTA Conference, Budapest, Akadémiai Kiadó, Budapest 1975.
18 J. Paulik and F. Paulik, J. Thermal Anal., 8 (1975) 557.
19 F. Paulik, J. Paulik, R. Naumann, K. Köhnke and D. Petzold, Thermochim. Acta, 64 (1983) 1.
20 F. Paulik, J. Paulik and K. Wieczorek-Ciurowa, J. Thermal Anal., 28 (1983) 395.