

# Differential thermal analysis under quasi-isothermal, quasi-isobaric conditions (Q-DTA)

## Part II. Water evaporation and the decomposition mechanism of compounds with structural and crystal water

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### Abstract

It is already a generally accepted opinion today that the course of DTA, DSC and TG curves is deteriorated by the non-isothermal heating control and by other experimental conditions to such an extent that it is more characteristic for the experimental conditions, than for the transformation itself.

This problem can be eliminated completely by the simultaneous use of “transformation-governed heating control” (TGHC) and “self-generated atmosphere” (SGA) ensuring quasi-isothermal, quasi-isobaric conditions for the DTA measuring technique (Q-DTA).

This experience is proven on the examples of the evaporation of water under boiling, the dehydration of  $\text{Ca}(\text{OH})_2$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mg}(\text{OH})_2$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  by providing both, the results obtained by the DTA, TG and the Q-DTA measuring techniques. © 2004 Elsevier B.V. All rights reserved.

*Keywords:* Q-DTA; Q-TG method; Quasi performing the thermodynamic claims; Quasi-static; TGHC; CRTA heating control

### 1. Introduction

The course of physical and chemical transformations under ideal conditions strictly regulated by thermodynamical laws are more or less deteriorated by the circumstances under traditional DTA, DSC investigations (shape of the sample holder, amount of the sample, etc.), and by the non-isothermal heating programme. This is the reason why the characteristic temperature and transformation heat values determined from the area under the peaks of DTA, DSC curves published often differ significantly. The course of these curves is consequently non-isothermal, even when according to thermodynamic laws—the course of the transformation is isothermal. The resolution and selectivity of the curves is generally too small, therefore the interpretation and quantitative evaluation of the curves is often difficult [1].

In order to eliminate these problems, earlier measuring techniques having the collective name of “quasi-static” were

introduced. The methods Q-DTA, Q-TG [1] belong to these techniques.

The operation of the equipment used for the simultaneous Q-DTA, Q-TG method [2–4], as well as the principle on which this method eliminates the above problems is described in detail in earlier publications. This paper is intended to show on the example of water and some water-containing compounds how the novel course of the  $\text{Q-TA}_{T_s^n}$  and  $\text{Q-TG}_{T_s^n}$  curves taken by this new method should be interpreted and quantitatively evaluated, which courses are totally different from the course of traditional DTA and TG curves.

### 2. Experimental

In addition to the “school example” of water evaporation (Figs. 1–3), the dehydration of  $\text{Ca}(\text{OH})_2$  (Fig. 4),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Fig. 5),  $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$  (Fig. 6),  $\text{Mg}(\text{OH})_2$  (Fig. 7) and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (Fig. 8) was also investigated. Experiments were carried out by the instrument Derivatograph

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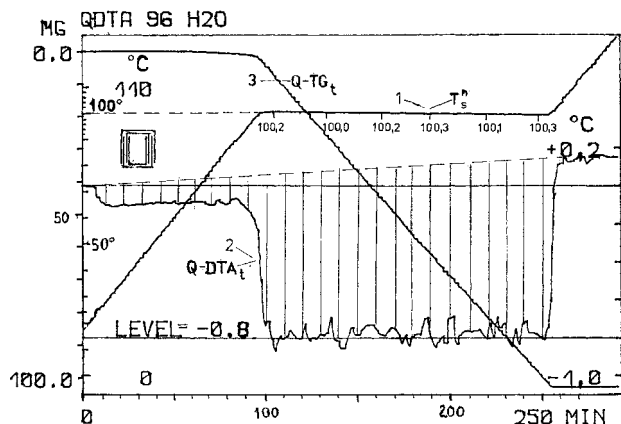


Fig. 1. Evaporation of water under boiling. Original record. Examined under "normal" conditions by the Q-DTA method.

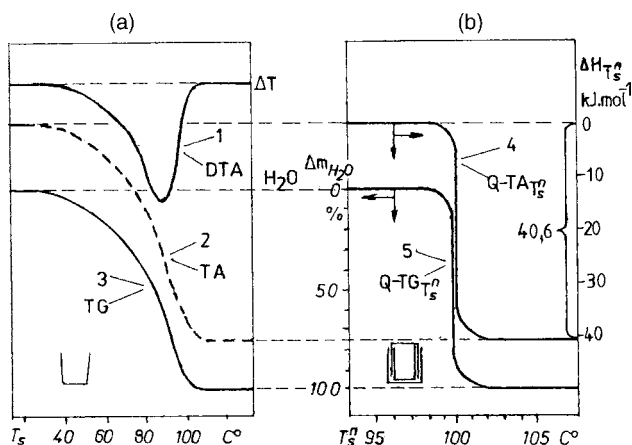


Fig. 2. Evaporation of water under boiling. Examined by the conventional DTA, TG (a) and by the Q-DTA, Q-TG (b) methods.

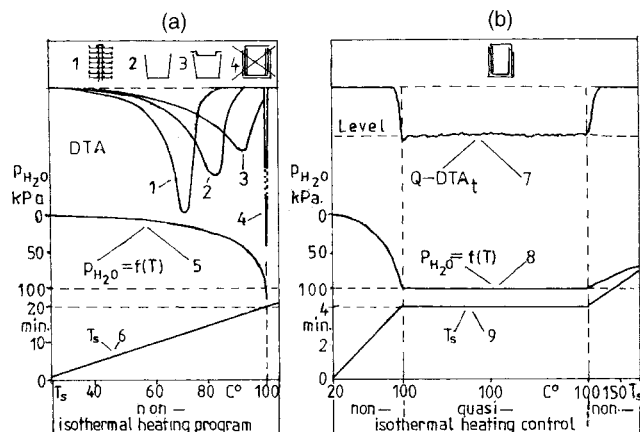


Fig. 3. Changes in the courses of curves at the examination of water by using the DTA (a) and Q-DTA (b) methods. DTA (curves 1–4), Q-DTA (curve 7), changes in the partial pressure of the water vapour (curves 5, 8) and in the sample temperature (curves 6, 9).

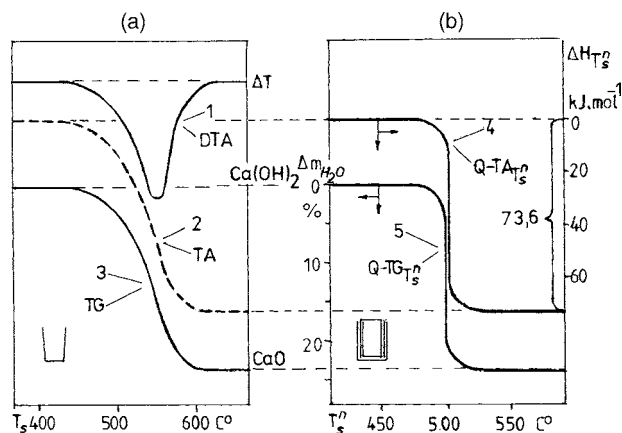


Fig. 4. Dehydroxylation of  $\text{Ca}(\text{OH})_2$ . Results of conventional (part a) and Q-DTA (part b) examinations.

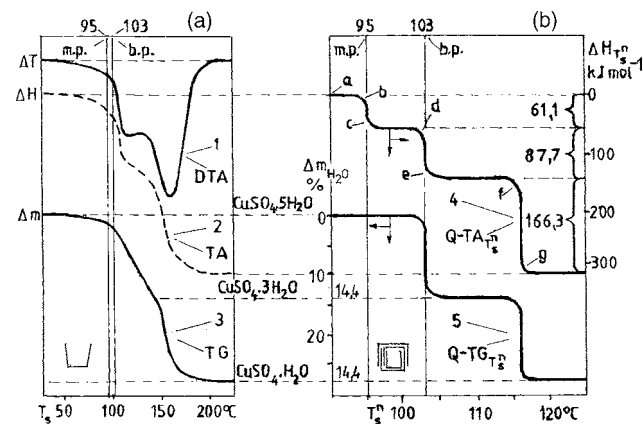


Fig. 5. Dehydration of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Results of conventional (part a) and Q-DTA (part b) examinations.

C (Hungarian Optical Works (MOM), Budapest). This instrument has originally been applicable to perform traditional, simultaneous TG, DTG, DTA, EGA [1] and "quasi-isothermal, quasi-isobaric thermogravimetry (Q-TG) measurements [1] alternately, but it was made suitable later also for performing the "quasi-isothermal, quasi-isobaric

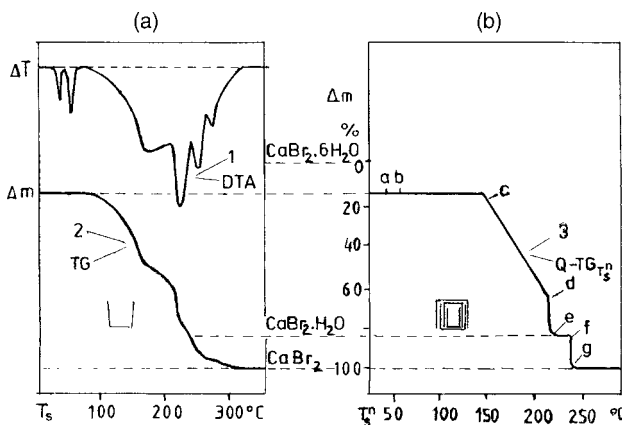


Fig. 6. Dehydration of  $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$ . Results of conventional (part a) and Q-DTA (part b) examinations.

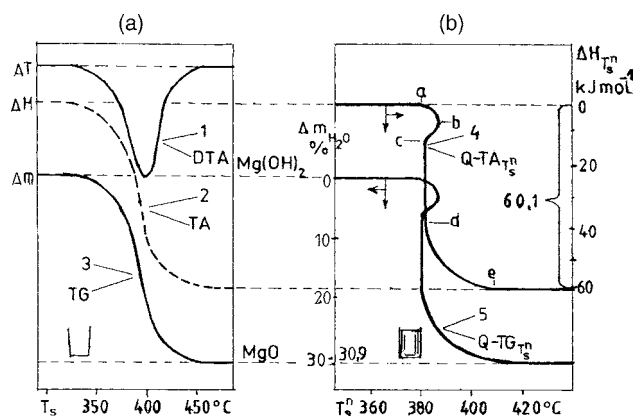


Fig. 7. Dehydroxylation of  $\text{Mg}(\text{OH})_2$ . Results of conventional (part a) and Q-DTA (part b) examinations.

differential thermal analysis” studies (Q-DTA), as well [2–4].

By using the latter equipment, the “normal” (n) evaporation heat of water under boiling, and its course were determined. Results are illustrated in Fig. 1 (original record). In this Figure, curve Q-DTA<sub>t</sub> (curve 2) shows how the enthalpy ( $\Delta H$ ) of the sample (s) changed in function of time ( $t$ ). The change in the sample weight can be followed in curve 3 (Q-TG<sub>t</sub>), whereas that of sample temperature ( $T_s^n$ ) in curve 1.

Two remarks concerning the original record (Fig. 1):

The heating control system switched from the non-isothermal operation mode to quasi-isothermal one only when the temperature of the water reached 100 °C, because the deviation of the Q-DTA signal did not reach the “level” before 100 °C due to the small heat capacity of water, thus it could not bring the heating control system into operation.

Temperature values given beside the individual points of curve 1 ( $T_s^n$  curve) could not have been read from the curve itself with sufficient accuracy. They were determined from the data in the memory of the computer individually.

The constructed Fig. 3 is intended to visualize the supposed mechanisms of water evaporation under the experimental conditions of traditional DTA investigation (Fig. 3a) and that taking place at the application of the quasi-isothermal conditions of the Q-DTA measurement (Fig. 3b). DTA curves (curves 1–4) are taken by using the traditional sample holder consisting of plates [1a] (curve 1) and by uncovered (curve 2), covered (curve 3) and labyrinth [1b] (curve 4) crucibles, and with non-isothermal heating control, whereas the Q-DTA<sub>t</sub> curve (curve 7) was recorded by applying the labyrinth sample holder [1b] and quasi-isothermal heating [1c,3,4] introduced by non-isothermal heating. Curves 5 and 8 illustrate the change of the equilibrium pressure of water vapour ( $p_{\text{H}_2\text{O}}$ ) determining the course of transformations in function of the change in sample temperature ( $T_s$ ) ( $p_{\text{H}_2\text{O}} = f(T)$ ) (curves 6, 9). The labyrinth crucible could not be used for DTA studies, as the fast increasing vapour and/or gas pressure would push out the crucible. Thus, the course of curve 4 is not real, only hypothetical.

On sides “b” of Figs. 2–5, 7 and 8 are shown the results of the Q-DTA measurements, the Q-TA <sub>$T_s^n$</sub>  (curves 4) and the Q-TG <sub>$T_s^n$</sub>  (curves 5). On sides “a” of the same figures, the DTA (curve 1) and TG (curve 3) curves of the same compounds taken under the conditions of the traditional DTA method are shown, in order to illustrate the advantages of the new measuring technique as compared to the traditional one. The comparison of curve pairs TG–Q-TG <sub>$T_s^n$</sub>  was possible without any difficulty, whereas curve pairs DTA–Q-TA <sub>$T_s^n$</sub>  could not be easily compared. Therefore, the DTA curves have been integrated graphically, and the TA curves thus constructed (curve 3) have also been shown together with the DTA curves. The direct comparison of the TA and Q-TA <sub>$T_s^n$</sub>  curves became thereby already possible.

The Q-TA <sub>$T_s^n$</sub>  curves in Figs. 2b, 4b, 5b, 7b and 8b show the enthalpy changes ( $\Delta H_{T_s^n}$ ) measured in the experiments. If the transformation was a multistep one, the values of

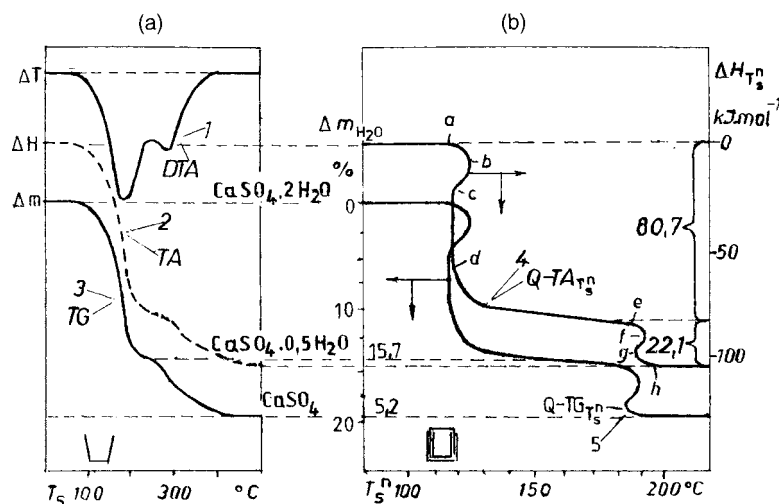


Fig. 8. Dehydration of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Results of conventional (part a) and Q-DTA (part b) examinations.

enthalpy change for the individual steps are also shown (Fig. 5b). However, it should be noticed that these values of the enthalpy changes are necessarily different as compared with the so-called normal transformation heats calculated from the normal formation heats ( $\Delta H_{298\text{K}}^0$ ) found in physico-chemical tables [5].

This value differs also from the enthalpy change values ( $\Delta H_{T_1}$ ,  $\Delta H_{T_2}$ ,  $\Delta H_{T_3}$ , ...) measured by the DTA or DSC method under different experimental conditions, and, as a consequence, at different temperatures ( $T_1$ ,  $T_2$ ,  $T_3$ , ...) as well [2]. The difference is caused by the fact that the value of transformation heat changes with temperature (Kirchhoff's rule). The difference can be proved even numerically, if we consider that the formation heat of compounds does also change with the temperature, which recently has been also published in some physico-chemical tables [6].

### 3. Discussion

#### 3.1. Simple, ideal transformations free of foreign processes

The question may arise, why and how can one provide such experimental conditions by the Q-DTA measuring technique under which the transformation studied occurs in the "normal" way, corresponding to the laws of physical chemistry. This question can be answered only by studying compounds which can be prepared with a theoretical composition, the physical or chemical transformation of which is unambiguous, without being influenced by other, foreign by-processes, e.g. by nucleus formation. Only very few such processes are known. The authors found earlier the modification change of  $\text{KClO}_4$ , and the heat decomposition of  $\text{CaCO}_3$  as such [2], therefore now the evaporation of water and the dehydroxylation of  $\text{Ca}(\text{OH})_2$  have been chosen.

#### 3.2. Evaporation of water under experimental conditions of the DTA method

A strange contradiction can be observed on the DTA curve in Fig. 2a. Its course is non-isothermal, in spite of the fact that it can be established that we have every reason to believe that the evaporation of water is a reversible process leading to equilibrium. However, the contradiction is only virtual. This is easy to see if the mechanism of evaporation during the DTA study is analyzed on the basis of Fig. 3a.

If the temperature ( $T_s$ ) of the sample (s) is increased by a constant rate (curve 6), then the equilibrium vapour pressure of water increases exponentially, according to function  $p_{\text{H}_2\text{O}} = f(T)$  (curve 5). Water vapour accumulates to the same degree in the very thin, film-like air layer being in direct contact with the water surface. Equilibrium is developed between the liquid water and the air-vapour mixture phases. From this layer, part of the water vapour leaves by diffusion corresponding to the ventilation conditions in the sample holder, which process leads also to equilibrium. In

the film-like layer, however, water vapour leaving to the environment is immediately made up for from the liquid phase.

The primary process follows the course of the vapour pressure-temperature relationship ( $p_{\text{H}_2\text{O}} = f(T)$ ). This function determines the range (in the present case 0–100 °C and 0–100 kPa) within which evaporation can take place. The secondary, diffusion process is regulated by the experimental conditions, by the measure of the enthalpy change, the non-isothermal heating rate, the form of the sample holder, the amount of the sample, etc. This secondary process defines the position of the DTA curve within the 0–100 °C range (Fig. 3a, curves 1–4), as well as the amplitude of curves and the range of the characteristic temperature ( $T^{\text{onset}}$ ,  $T^{\text{max}}$ ,  $T^{\text{offset}}$ ). This means that this secondary process deteriorates the course of the curves and makes it non-isothermal.

Between the mechanisms of the water evaporation and the decomposition of pure inorganic compounds ( $\text{CaCO}_3$ ,  $\text{Ca}(\text{OH})_2$ , etc.) free of side-processes a full analogy exists, with the exception that in the latter cases the transformation takes place according to the equilibrium decomposition pressure-temperature relationship, instead of the water vapour pressure-temperature relationship.

#### 3.3. Evaporation of water under the experimental conditions of the Q-DTA method

In elaborating the Q-DTA method, the inventors drew the conclusions from the above [2,3]. Investigations were carried out by applying the labyrinth sample holder [1b] ensuring a quasi 100% pure, "self-generated atmosphere" (SGA), which the water vapour could leave according to Fig. 3b, when the water started to boil (curves 7, 9), i.e. when the equilibrium vapour pressure of the water reached 100 kPa (curve 8).

Evaporation during boiling required a significant amount of heat. The initial point of enthalpy change was sensed by the DTA circuit. When the voltage of the DTA signal reached the value chosen in advance (level), the relay switch commanded the heating control to change from non-isothermal heating mode to the quasi-isothermal one [1c], i.e. to "transformation-governed heating control" [2,3].

After that, on the principle of feed-back, the heating control created a temperature difference between the sample and the furnace suitable for evaporating water with a very small and strictly constant rate (e.g. in case of Fig. 1  $0.25 \text{ kJ mol}^{-1}$ , i.e.  $0.6 \text{ g min}^{-1} \text{ mol}^{-1}$ ).

Interpretation and evaluation of the Q-DTA<sub>r</sub> curve (Fig. 1, curve 2) is even more difficult than that of the traditional DTA curve. This problem was overcome by developing further the Q-DTA instrument. According to the invention of the authors [4], the transformed instrument divides the Q-DTA<sub>r</sub> signal into two parts, in an accurately known ratio. One part of the signal is used further on for governing the heating control system. The other part of the signal is integrated providing thereby a new, until now not used

function of the enthalpy change (Q-TA<sub>T</sub>), and brings it to a common denominator with the function of weight change (Q-TG<sub>T</sub>). Subsequently both signals are transformed into the function of the “normal” temperature ( $T_s^n$ ) (curve 3) of the sample. This way curves Q-TA<sub>T<sub>s</sub><sup>n</sup></sub> and Q-TG<sub>T<sub>s</sub><sup>n</sup></sub> (curves 4, 5 in Fig. 2b) have been obtained. This procedure is performed by the corresponding software of the computer of the Q-DTA instrument, complemented with the command that before recording the transformed signals, it should multiply them with the calibration of the instrument and other stoichiometric factors.

From the curves Q-TA<sub>T<sub>s</sub><sup>n</sup></sub> and Q-TG<sub>T<sub>s</sub><sup>n</sup></sub> thus obtained (Figs 2b, 4b, 5b, 7b and 8b) every information and data can be read, therefore in what follows, only these curves will be provided as the end result of investigations.

The Q-DTA instrument was calibrated by the enthalpy change during the modification change of KClO<sub>4</sub>. The area under the Q-DTA<sub>T</sub> curve between 20 and 100 °C (Fig. 1, curve 2) corresponds to an enthalpy change of  $\Delta H_{T_s=20-100^\circ\text{C}} = 3.6 \text{ kJ mol}^{-1}$ , which is proportional to the heat capacity of the sample. No water vapour is left in this temperature interval, as is proven by the course of the curves Q-TG<sub>T</sub> (Fig. 1, curve 3) and Q-TG<sub>T<sub>s</sub><sup>n</sup></sub> (Fig. 2b, curve 6). This non-isothermal curve section of a relatively small slope is not shown on curve 4 in Fig. 2b.

After signal Q-DTA<sub>T</sub> (Fig. 1, curve 2) reached “level”, the leaving of 100 mg of water took place with a rate of  $0.6 \text{ mg min}^{-1}$ , in 170 min, in an isothermal way, at  $100.1 \pm 0.2^\circ\text{C}$ . The evaporation heat (under boiling) readable from curve Q-TA<sub>T<sub>s</sub><sup>n</sup></sub> (Fig. 2b, curve 4) was found to be  $\Delta H_{T_s=100^\circ\text{C}} = 40.6 \text{ kJ mol}^{-1}$ .

### 3.4. Decomposition of Ca(OH)<sub>2</sub> under the experimental conditions of the DTA and Q-DTA methods

At comparing Figs. 2 and 4 it turns out that there is a similarity between the courses of TA, TG and Q-TA<sub>T<sub>s</sub><sup>n</sup></sub>, Q-TG<sub>T<sub>s</sub><sup>n</sup></sub> curves. The TA, TG curves show both evaporation and dehydroxylation processes to be non-isothermal (Figs. 2a and 4a), in spite of both being obviously reversible processes.

However, the course of curves Q-TA<sub>T<sub>s</sub><sup>n</sup></sub>, Q-TG<sub>T<sub>s</sub><sup>n</sup></sub> can be in both cases qualified as isothermal. The transformation temperature, the enthalpy change of the transformation, in general the course of the curves are changed in both cases, for water and Ca(OH)<sub>2</sub> as well, even if the investigations were repeated under changed conditions, e.g. with changing the amount of the sample or the rate of the transformation, etc.

This observation can be generalized and extended for all reversible transformations of inorganic compounds of stoichiometric composition if the process is free of side reactions (see Section 6).

The values of enthalpy change  $\Delta H_{T_s=500^\circ\text{C}} = 73.6 \text{ kJ mol}^{-1}$  and characteristic temperature ( $T_s^n = 500^\circ\text{C}$  of Ca(OH)<sub>2</sub> readable from these curves agree practically with

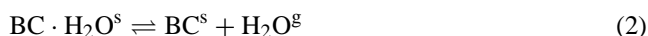
other values determined by other physico-chemical methods which can be accepted as theoretical data in the literature.

## 4. Decomposition mechanism of compounds containing crystal or structural water

These compounds can be classified into two basic classes according to their decomposition mechanism.

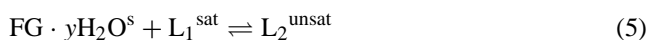
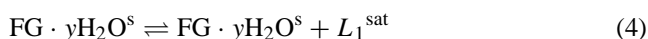
### 4.1. Decomposition to a solid and a gaseous phase

Some compounds containing crystal (e.g. CaSO<sub>4</sub>·2H<sub>2</sub>O [1h]) and structural water (e.g. Mg(OH)<sub>2</sub> [1j], Ca(OH)<sub>2</sub>), decompose to a solid (s) and a water vapour (g) phase (Figs. 4b, 7b and 8b).



### 4.2. Congruent and incongruent transformations of salt hydrates

At heating, some salt hydrates dissolve totally, congruently in their own crystal water Eq. (3), whereas others only partially, incongruently Eq. (4). In case of incongruently dissolving salt hydrates more incongruent steps, or at the end a congruent dissolution may follow each other Eq. (5).



#### 4.2.1. Decomposition mechanism of congruent and incongruent transformations under the experimental conditions of DTA, TG method

At studying the latter systems by the traditional DTA, TG method, in addition to state modification, they undergo also other changes. The steadily increasing temperature ( $T$ ) shifts the equilibrium of such systems to the reduction of solution concentration. Application of the traditional open sample holder-at increasing the temperature-leads to a water loss due to evaporation (–H<sub>2</sub>O). The resultant of the common effects of these two antagonistic processes  $\xrightarrow[-\text{H}_2\text{O}]{<T<} \rightarrow$  and the experimental conditions are the DTA, TG curves (Figs. 5a and 6a).

As is shown in Fig. 3a (curves 1–4), the slightest change in the experimental conditions of traditional experiments is capable of influencing significantly even the course of the evaporation of pure water. Thus it is understandable that the in se complex process of water loss from salt hydrates is made almost uninterpretable by these effects (Figs. 5a and 6a).

#### 4.2.2. Decomposition mechanism of compounds containing crystal or structural water under experimental conditions of the Q-DTA, Q-TG method

To the contrary of water evaporation under boiling, the water loss of these compounds is a complex process. The steps of this process may be totally different, e.g. one of them might be isothermal, whereas the subsequent step might be non-isothermal (Fig. 6b). In order to have both steps to occur under normal conditions, the program of the control system should be adjusted automatically to this fact, e.g. the heating control, after the non-isothermal step had started, should increase it by the appropriate rate.

Traditional DTA, DSC or TG methods are unsuitable for changing the program automatically, this can only be done by using “transformation-governed heating control” and “self-generated atmosphere” simultaneously (Conclusion 6).

The Q-DTA instrument changes its heating program automatically even when the two steps are not tightly following each other. In this case, when the first step is finished, the heating control switches back automatically to the non-isothermal heating mode, and the quasi-isothermal heating control starts again only when the next step of the transformation starts (Fig. 5b).

The new phase may be porous ( $\text{CaCO}_3$ ) [1d], but it may also be solid, delaying thereby the leaving of the gaseous decomposition product by diffusion. The increase in the layer thickness of such a new phase would decrease the rate of the isothermal transformation, if the heating control had not increased the temperature of the sample. In order to keep the transformation rate constant, the Q-DTA instrument has to increase the temperature automatically. The sections of curves  $Q\text{-TA}_{T_s^n}$  and  $Q\text{-TG}_{T_s^n}$  change to non-isothermal, but the equilibrium nature of the transformation remains preserved (Figs. 7b and 8b) [1e] (Conclusion 3).

The transformation starts often by nucleus formation. When such a process is started, only a few nuclei are formed on the surface of the crystals, too few to let the transformation take place with the chosen rate. This condition brings the relay system into operation, and it forces the heating control system to raise the temperature of the sample to the desired extent. Later on, when more nuclei were formed than needed, the heating control system decreases the sample temperature automatically to the “normal” value, at which the transformation takes place under equilibrium conditions, with the very small and constant, predetermined rate. This process produces at the beginning of the  $Q\text{-TA}_{T_s^n}$  and  $Q\text{-TG}_{T_s^n}$  curves a beak-formed part (Figs. 7b and 8b) [1f] (Conclusion 3).

The labyrinth sample holder ensures developing the “self-generated atmosphere” (SGA). It realizes this fully automatically and with a large flexibility, like the TGHC.

In the case of reaction of the type  $AB^s \rightleftharpoons A^s + B^g$ , the labyrinth sample holder ensures an SGA of 100% purity and 100 kPa partial pressure of water vapour continuously, thus this type of transformations takes place at a well-defined,

so-called “normal” temperature and in an isothermal way (Fig. 5b) [1b,1g] (Conclusion 1).

Water vapour leaves unsaturated solutions only when the temperature of the solution reaches the boiling temperature corresponding to its concentration. From this point on, the boiling point of the solution increases correspondingly to the leave of water vapour or the concentration increase of the solution, until the solution becomes saturated (Fig. 6, curve 3, section c–d) [1h] (Conclusion 5).

The water loss of saturated solutions starts when its temperature reaches the boiling point corresponding to its concentration. However, the temperature of the solution does not change until the total evaporation, since in the mean time, a solid intermediate salt hydrate or water-free salt precipitates from the solution, the amount of which is proportional with the amount of water vapour that leaves (Fig. 6b, curve 3, section d–e) [1h] (Conclusion 5).

#### 4.2.3. Decomposition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Though the heat decomposition of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is a multistep transformation [1i], but it is free of foreign processes (e.g. nucleus formation), therefore the course of the  $Q\text{-TA}_{T_s^n}$  and  $Q\text{-TG}_{T_s^n}$  curves (Fig. 5b) taken at the normal conditions of the Q-DTA method can be considered ideal and well interpretable.

According to the course of these curves, at 95 °C (point b), the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  melted incongruently (point b), and solid  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  intermediate and a small amount of saturated solution was formed Eq. (4). This process was strictly isothermal (b–c). The saturated solution contained a relatively small amount of dissolved salt, thus it started to boil already at 103 °C (point d). During boiling (d–e), an amount of dissolved  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  proportional to the amount of water vapour removed from the saturated solution precipitated, thus the boiling temperature remained constant. At the end of this process (e) only solid tri-hydrate was present, which in the sense of Eq. (2), decomposed isothermally at 116 °C, at the formation of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  and water vapour (f–g).

When comparing the curves in Fig. 5a and b it can be established that the resolution power and selectivity of the traditional DTA method do not approach those of the Q-DTA measuring technique (Conclusions 6, 7, 8).

It could also be read from the  $Q\text{-TA}_{T_s^n}$  curve that the following enthalpy changes occurred:

$$\Delta H_{T_s^n=95^\circ\text{C}} = 61.1 \text{ kJ mol}^{-1} \text{ for the incongruent melting;}$$

$$\Delta H_{T_s^n=103^\circ\text{C}} = 87.7 \text{ kJ mol}^{-1} \text{ for the concentration of the saturated solution;}$$

$$\Delta H_{T_s^n=116^\circ\text{C}} = 166.3 \text{ kJ mol}^{-1} \text{ for the decomposition of } \text{CuSO}_4 \cdot 3\text{H}_2\text{O} \text{ to } \text{CuSO}_4 \cdot \text{H}_2\text{O}.$$

#### 4.2.4. Decomposition of $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$

The heat decomposition of  $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$  has already been studied earlier [7] by means of the Q-TG method. Though the course of the Q-TG $_{T_s^n}$  curve is not suitable for determining the enthalpy changes accompanying the heat decomposition of the sample, the process of water loss from the sample can be interpreted from the curve (Fig. 6, curve 3).

Thus, it can be established on the basis of this curve e.g. that in spite of the temperature of the unsaturated solution (curve section b–c) being well above 100 °C, due to the use of the labyrinth crucible, the weight of the sample remained constant up to 140 °C (c). The solution started to boil at 140 °C. After that (c–d), the system lost water gradually, and proportionally to this, the boiling temperature increased. The solution became saturated at 214 °C (d). The solution boiled further, lost water, but its boiling point did not increase further, as the concentration of the solution remained constant (d–e). Namely, in a proportional amount to the water loss, solid mono-hydrate intermediate precipitated. At the point “e” the solution phase disappeared. The remaining solid  $\text{CaBr}_2 \cdot \text{H}_2\text{O}$  decomposed isothermally (f–g) at 240 °C according to Eq. (2).

Summing up it can be established that to the contrary of traditional DTA, DSC or TG methods (Figs. 5a and 6a), or static calorimetric measurements, by using the Q-DTA measuring technique the individual steps of the congruent or incongruent melting of salt hydrates, as well as those of the evaporation of saturated or unsaturated solutions can be very well distinguished (Figs. 5b and 6b), and their course, together with the accompanying enthalpy changes (Fig. 5b curve 4), can be determined under normalized conditions (Conclusions 5–8).

### 5. Decomposition to a solid and a gaseous phase accompanied by foreign processes

Decomposition of compounds containing crystal or structural water Eqs. (1) and (2) leads to equilibrium governed by the decomposition pressure–temperature relationship. As a general rule, we can state that if the Q-TA $_{T_s^n}$  or Q-TG $_{T_s^n}$  curves of the compounds belonging to this group are only partly of isothermal course (Figs. 7b and 8b), then it should be supposed that the non-isothermal section of the curves is modified by other, additional physical or chemical processes (e.g. nucleus formation, or formation of a new solid phase), but without modifying its character leading to dehydration equilibrium. This section of the curves is the resultant of the effects of the two different processes [1e,1f]. According to experience, only very few decomposition reactions are free of such secondary effects.

#### 5.1. Dehydroxylation of $\text{Mg}(\text{OH})_2$

At first sight, the course of curves 4, 5 in Fig. 7 makes the false impression that the dehydroxylation of  $\text{Mg}(\text{OH})_2$  does not lead to equilibrium. However, the short strictly

isothermal section, c–d, of the Q-TA $_{T_s^n}$  and Q-TG $_{T_s^n}$  curves proves unambiguously that the dehydroxylation of  $\text{Mg}(\text{OH})_2$  is a process leading to equilibrium.

However, a beak-like section is also present on these curves (points a, b, c) what is a sure sign of a delayed start of nucleus formation [3f]. The loss of structural water is an isothermal process (c, d), whereas the second part of the curve indicates the presence of a non-isothermal process (d, e). The reason for this might be that the new phase ( $\text{MgO}$ ) formed on the surface of the crystal particles was porous to such an extent that initially water vapour could diffuse through the particles without any resistance, but later on, the resistance increased with the increasing thickness of the new phase [3d] (Conclusion 3).

The enthalpy change due to the dehydroxylation of  $\text{Mg}(\text{OH})_2$  measured under normal conditions ( $\Delta H_{T_s^n=380^\circ\text{C}}$ ) was found to be 60.1 kJ mol<sup>-1</sup>.

#### 5.2. Decomposition of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

From the course of the Q-TA $_{T_s^n}$  and Q-TG $_{T_s^n}$  curves (Fig. 8b, curves 4, 5) it turns out that dehydration of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is also introduced by nucleus formation (points a, b, c). After this process had been finished, the leave of about 1 mol of crystal water occurs under strictly isothermal conditions, at 120 °C (c, d). At the continuation of the equilibrium formation of the hemi-hydrate (d, e), the temperature of the sample increases faster and faster. This is why, similarly to  $\text{Mg}(\text{OH})_2$ , the resistance of the new phase on the surface of crystal particles against vapour diffusion increases. The decomposition of  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  in a pure water vapour atmosphere is also introduced by a delayed nucleus formation (e, f, g). The first section of dehydration caused an enthalpy change  $\Delta H_{T_s^n=120^\circ\text{C}} = 80.7$  kJ mol<sup>-1</sup>, whereas that of the second section has been found to be  $\Delta H_{T_s^n=185^\circ\text{C}} = 22.1$  kJ mol<sup>-1</sup> (Conclusion 3).

### 6. Conclusions

1. By using the simultaneous Q-DTA, Q-TG method with the application of both “transformation-governed heating control” (TGHC) and pure “self-generated atmosphere” (SGA), the requirements set by thermodynamics can be satisfied sufficiently.
2. At repeating the study of the reversible transformations of inorganic compounds free of foreign elementary processes, the Q-DTA instrument provides consequently the same characteristic temperature and enthalpy change both being near to the theoretical value, as well as it records consequently the same isothermal course of the Q-TA $_{T_s^n}$  and Q-TG $_{T_s^n}$  curves also near to the theoretical course.
3. If the course of the Q-TA $_{T_s^n}$  and Q-TG $_{T_s^n}$  curves of pure compounds differed partly or totally from the isothermal course, it would allow for the conclusion that the

isothermal transformation is accompanied by another elementary chemical or physical process (e.g. nucleus formation).

4. The non-isothermal course of curves  $Q-TA_{T_s^n}$  and  $Q-TG_{T_s^n}$  of not reversible reactions (decomposition of plastics, organic compounds, solid phase inorganic reactions, etc.) can be influenced only by active gases (e.g. oxygen). By using the TGHC method, however, the course of the curves becomes characteristic for the material, and at repeating the experiment, it remains consequently unchanged.
5. By applying the labyrinth crucible, water or aqueous salt solutions loose water only at the boiling temperature. The boiling temperature of the unsaturated solution increases with losing water, whereas that of the saturated solution remains constant.
6. The course of the traditional DTA curves is always non-isothermal, independently whether the transformation is reversible or not. The isothermal and non-isothermal sections of the  $Q-TA_{T_s^n}$  and  $Q-TG_{T_s^n}$  curves can always be distinguished which makes the interpretation and quantitative evaluation of these curves easier.
7. The resolution power and selectivity of the Q-DTA technique is significantly superior to those of the traditional methods.
8. Enthalpy changes belonging to the partial processes of transformations could be determined by a sufficient accuracy by the Q-DTA technique. By the use of the course of traditional DTA curves, these values could only be estimated approximately, and by applying static calorimetric measurements, they could not be determined at all.

### 7. A summary of the so-called quasi-static methods [8]

1. *Quasi-isothermal TG (Q-TG)*. This was the first quasi-static method. Introduction of the method of “transformation-governed heating control” (TGHC). The heating of the thermobalance was governed by the Q-DTG signal. F. Paulik, J. Paulik, L. Erdey 1962.
2. *Constant rate TA (CRTA)*. Heating of the evacuated instrument was governed by the pressure change of the gaseous product, and the change in the temperature was measured by a thermocouple. The apparatus was used for studying solid phase reactions. J. Rouquerol, 1964.
3. *DTA instrument using simple electromechanical heating control*. It was used for measuring transformation temperatures. C.M. Beam, R.H. Oliver, 1967.
4. *Constant decomposition rate TG (CRTA)*. Heating regulation of vacuum thermobalances governed by the pressure change of the gaseous product. J. Rouquerol, 1969.
5. *Quasi-isothermal, quasi-isobaric simultaneous TG, DTA, EGA*. Introduction of the simultaneous application of the TGHC heating control and SGA self-generated atmosphere (labyrinth crucible), and industrial realization of the apparatus working under normalized conditions. Heating control is governed by the Q-DTG signal. F. Paulik, J. Paulik, 1973.
6. *Quasi-isothermal TD (Q-TD)*. Thermodilatation study by using TGHC heating control. The heating was governed by the Q-T signal. J. Paulik, F. Paulik, 1977.
7. *Stepwise isothermal TD*. The regulation system periodically interrupted the heating of the dilatometer, and it was started again only when no dilatation occurred any more. O.T. Sorensen, 1978.
8. *Stepwise isothermal TG*. The heating of the thermobalance was periodically interrupted by the regulating system, and it was started again only when no weight change occurred any more, O.T. Sorensen, 1980.
9. *Quasi-isothermal, quasi-isobaric simultaneous DTA, TG (Q-DTA, Q-TG)*. Normalized conditions were ensured by the simultaneous application of the TGHC heating control and “self-generated atmosphere” (SGA, labyrinth crucible). Heating was controlled by the Q-DTA signal. This heating control could be applied also in DSC. The procedure is realized industrially as well. F. Paulik, J. Paulik, M. Arnold, 1985. Further developed by: F. Paulik, E. Besseney-Paulik, K. Walther-Paulik, 1995.

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