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

Part III. Mechanism of congruent and incongruent phase transformations of salt hydrates

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Abstract

By using the "*simultaneous* Q-DTA, Q-TG *measuring technique*" elaborated recently, conditions near to the requirements of thermodynamics can be created, thus the "normalized" course of curves taken by this method, their characteristic temperatures or the values measured for the enthalpy change can be considered to be near to the theoretical values.

For testing this new method, $CuSO_4 \cdot 5H_2O$, $MnSO_4 \cdot 5H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $Na_2SO_4 \cdot 10H_2O$ have been investigated. These model substances can be prepared in stoichiometric composition free of impurities, their decomposition mechanism is well-known, thus the effect of the altered experimental conditions by the simultaneous Q-DTA, Q-TG method on the course of their dehydration can be calculated.

Keywords: Q-DTA and Q-TG measuring technique; Transformation-governed heating control (TGHC); Self-generated atmosphere (SGA)

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1. Introduction

The unusual name of "quasi-isothermal, quasi-isobaric measuring technique" (Q-TG, Q-EGA, Q-TD) [1–3] requires some explanation. This name should emphasize the fact that in these investigations a heating technique and a sample holder with a specific form are applied which are totally different from the traditional ones.

The authors of the Q-TG method [1–3] applied first the heating control named "*quasi-isothermal*" [1–4]. This method unifies the advantages of the traditional "*isothermal*" and "*non-isothermal*" heating control modes without having their disadvantages. The heating control with the name of "*quasi-static*" [2,6] represents a transition between "*static*" and "*dynamic*" heating control. This kind of heating control is also called "transformation-governed heating control" (TGHC) referring to its operation principle. This name is correct, as e.g. the heating control of the Q-TG instrument is governed by the strictly constant and very low temperature difference between the sample and the furnace by the feed-back principle, which difference is proportional to the heat flux, which in turn, is proportional to the heat absorbed, that is proportional to the rate of the transformation, being proportional to the change in the potential of the DTG signal.

The "*Q-TG method*" applying "*quasi-isothermal heating control*" [1–3] has already a past of four decades. After the application for the invention [4], more papers were published introducing measuring techniques (constant decomposition rate thermal analysis (CRTA) [7,8], stepwise isothermal analysis [9]) which, similarly to the Q-TG method, intended also to eliminate the disadvantages of the non-isothermal heating control, but they differed from it as well in the mode

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of heating control (heating mode governed by the change in the decomposition pressure under atmospheric depression, or alternately changing isothermal and non-isothermal heating mode, etc. [7–9]) as well as in experimental conditions, consequently also in the experimental results. Heating techniques not following the traditional way obtained the collective name of "*quasi-static*" methods [2,13].

The name "quasi-isobaric" used together with "quasi-isothermal" indicates that—instead of traditional open sample holders—a specific, so-called "*labyrinth*" sample holder [1,5] is used, from which, immediately at the start of decomposition, the decomposition products sweep along the air and prevent its flowing back. Thus the decomposition reactions can be studied at a constant pressure of 100 kPa of the so-called "*self-generated atmosphere*" (SGA).

The authors of the present paper applied a new, recently elaborated measuring technique in their investigations, the so-called "*simultaneous Q-DTA, Q-TG method*" [10–13]. This method differs from the Q-TG method used successfully earlier in two points. The heating control system of the simultaneous Q-DTA, Q-TG instrument is governed by the Q-DTA signal, i.e. by the rate of enthalpy change, and not by the Q-DTG signal (Fig. 1). The other point is that with this instrument, after its simple calibration, the enthalpy changes of transformations can be measured simply and accurately [6,12,13] (Fig. 2b). The principal basis for the method and the implementation of measurements are described in the first part (Part I) of this series [6].

If we want to prove that a task can be solved authentically by using a new measuring technique elaborated with the intention of improvement, then we have to study compounds preparable with a stoichiometric composition, and the crystal structure of which, as well as every detail of its decomposition mechanism are well known.

This is why the authors have chosen for this purpose salt hydrates containing structural and crystal water. These compounds, namely, seem to be suitable for testing the "*simultaneous Q-DTA, Q-TG method*". The results of these studies are provided in the second part (Part II) of this series [13].

In this paper, for the same purpose, the mechanisms of the congruent and incongruent transformations of several salt hydrates are studied. The results of these experiments are summarized in the present paper.

2. Experimental conditions

Dehydration of salt hydrates $CuSO_4{\cdot}5H_2O$ (Figs. 1 and 2), $MnSO_4{\cdot}5H_2O$ (Fig. 3), $Mg(NO_3)_2{\cdot}6H_2O$ (Fig. 4) and $Na_2SO_4{\cdot}10H_2O$ (Fig. 5) were studied, once by using the traditional simultaneous TG, DTG, DTA [1] method, and then by the simultaneous Q-DTA, Q-TG [12] method. Results of the former studies are shown at the left side of the figures (Figs. 2a–5a), whereas those of the latter are found at the right side of the same (Figs. 2b–5b).

Measurements were carried out by the instrument Derivatograph C (MOM, Hungarian Optical Works, Budapest), system Paulik, Paulik and Erdey. This instruments was fabricated originally for performing the "*simultaneous TG, DTG, DTA, EGA*" and in an alternative way, for the "*quasi-isthermal, quasi-isobaric thermogravimetric*" (Q-TG) measurements [1], but later it was made suitable for carrying out "*simultaneous Q-DTA, Q-TG*" [10–13] investigations, as well.

The "*simultaneous Q-DTA, Q-TG instrument*" is an adapter by which not only Derivatograph C is complemented, but it can be connected to any "*simultaneous TG, DTA instrument*" in an alternative way. This instrument is based on two inventions [10,11]. Fig. 1 was taken by the measuring technique according to the first invention [10], whereas Figs. 2b–5b according to the second one [11]. Fig. 1 is a not transformed, original curve, only some data are drawn on it

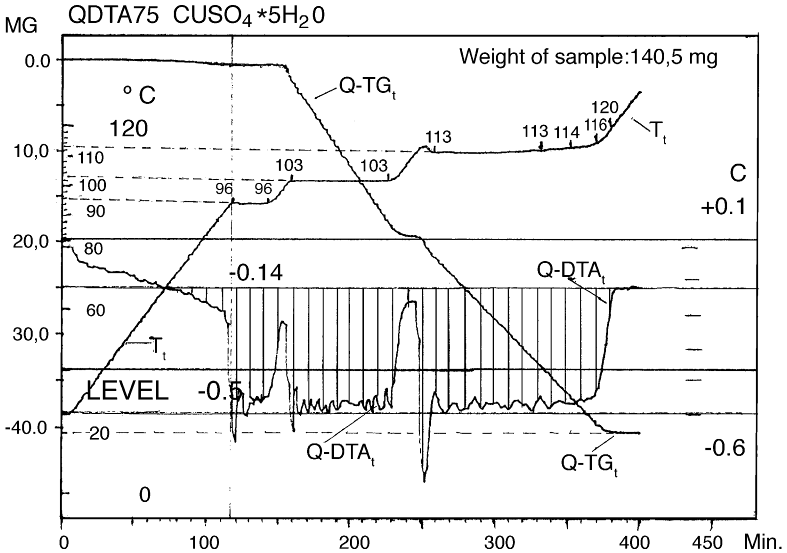

Fig. 1. Original record. Study of the dehydration of $CuSO_4{\cdot}5H_2O$.

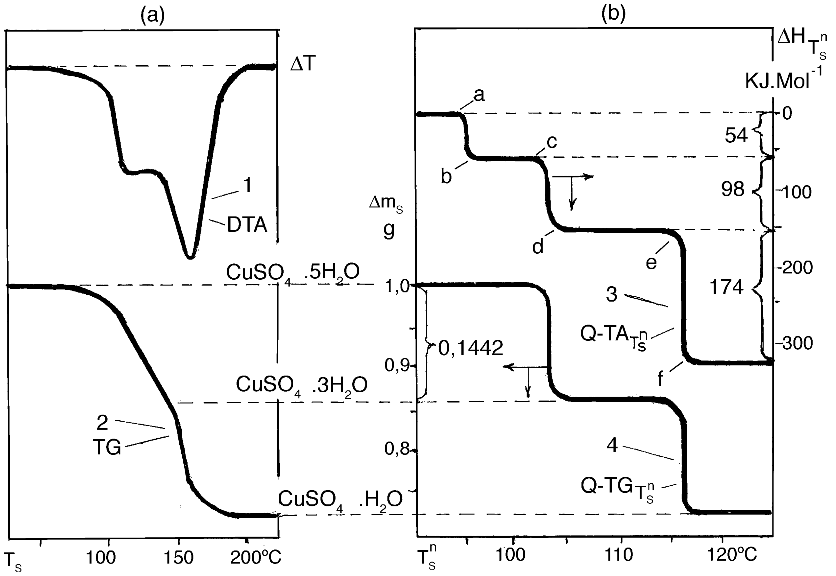

Fig. 2. Dehydration of $CuSO_4{\cdot}5H_2O$ studied by the traditional DTA, TG instrument (a) and by the simultaneous Q-DTA, Q-TG instrument (b).

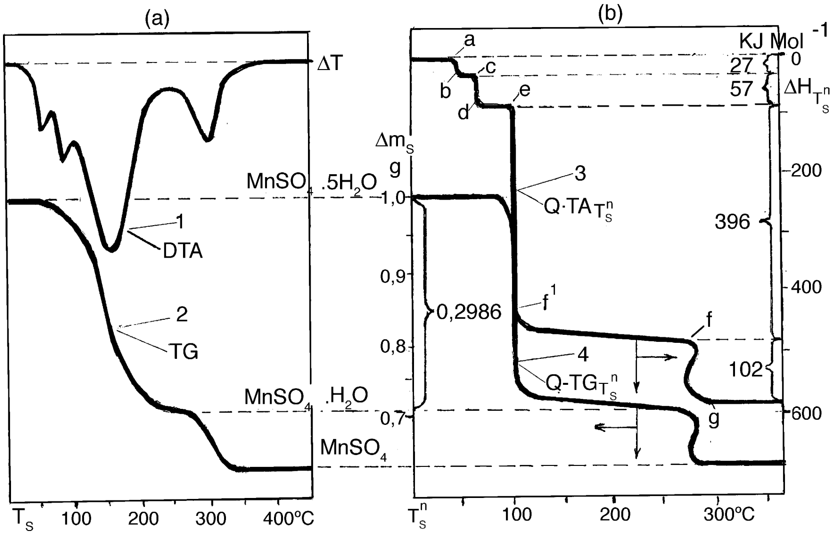

Fig. 3. Dehydration of $MnSO_4{\cdot}5H_2O$ studied by the traditional DTA, TG instrument (a) and by the simultaneous Q-DTA, Q-TG instrument (b).

later. In Fig. 1, taken according to invention in [10], i.e. by using "*transformation-governed heating control*" [1a,2,10] and in "*self-generated atmosphere*" [1b,2,10], the enthalpy change (curve Q-DTA$_t$), weight change (curve Q-TG$_t$) and temperature change (curve T_t) of the sample (s) is registered in function of time (t). The above curves are let to be registered by the adapter only for special request, otherwise only the end result of the measurement is registered, i.e. curves Q-TA$_{T_s^n}$ and Q-TG$_{T_s^n}$ are drawn which are more easy to interpret and can be more accurately evaluated.

The Q-TA$_{T_s^n}$ curves in Figs. 2b–5b provide the enthalpy change of the transformations in kJ mol^{-1}, whereas their course shows the course of the transformations under normalized (n) conditions in function of the sample (s) temperature (T_s^n).Q-TG$_{T_s^n}$ curves show the change in the weight of the samples (Δm_s) expressed in the weight change (g) of 1 g the sample, also as a function of sample temperature.

3. Dehydration of $CuSO_4{\cdot}5H_2O$

The Q-TA$_{T_s^n}$and Q-TG$_{T_s^n}$ curves taken by the simultaneous Q-DTA, Q-TG method shown in Fig. 2b illustrate the tearing down and removal of the first four crystal water molecules of $CuSO_4{\cdot}5H_2O$. According to curve 3, $CuSO_4{\cdot}5H_2O$ melted incongruently at 97 °C, and solid $CuSO_4{\cdot}3H_2O$ and a saturated solution (L_1^{sat}) were formed (Fig. 2b, curve 3, sections a–b). While the temperature increased from 97 to 103 °C, the saturated solution L_1^{sat} dissolved a further portion of $CuSO_4{\cdot}3H_2O$ (sections b–c). The

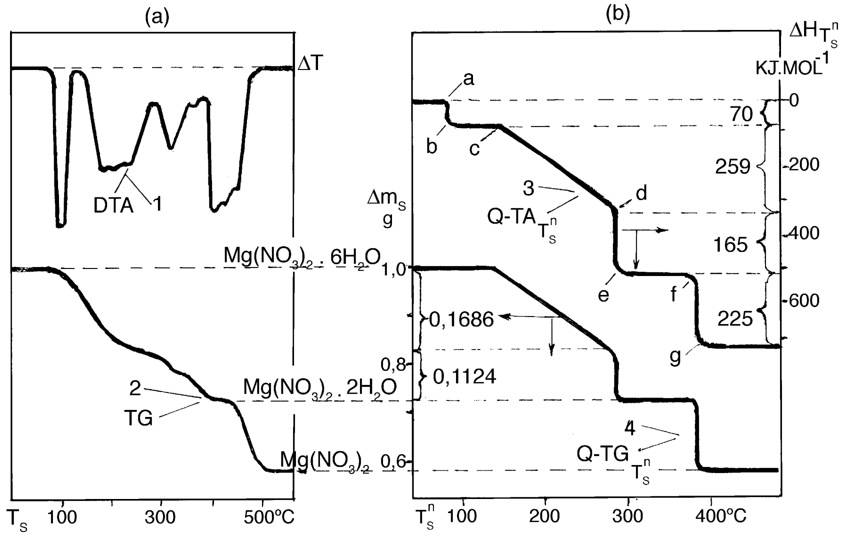

Fig. 4. Dehydration of $Mg(NO_3)_2 \cdot 6H_2O$ studied by the traditional DTA, TG instrument (a) and by the simultaneous Q-DTA, Q-TG instrument (b).

saturated solution L_2^{sat} started to boil at 103 °C, then, without a change in temperature, it evaporated, the intermediate $CuSO_4 \cdot 3H_2O$ crystallized out in its whole mass (sections c–d). The isothermal course of sections c–d in curve 3 proves that the solution L_2^{sat} remains saturated. During boiling, namely, simultaneously with the amount of water vapour leaving the system, an amount of $CuSO_4 \cdot 3H_2O$ proportional to the amount of the evaporated water was precipitated (sections c–d), thus till the end of the process the concentration, and consequently the boiling point of L_2^{sat} did not change. The intermediate solid $CuSO_4 \cdot 3H_2O$ decomposed to $CuSO_4 \cdot H_2O$ and water vapour at 116 °C (sections e–f).

The proper separation of the partial processes made it possible to determine the enthalpy changes of all the three partial processes from the course of the Q-TA$_{T_s^n}$ curve.

The fact that the solution L_2^{sat} contained only a relatively small amount of $CuSO_4 \cdot 3H_2O$ is made probable by its boiling point not being significantly different from that of water. Since the amount of $CuSO_4 \cdot 3H_2O$ held dissolved in L_2^{sat} was small, the dissolution heat might also be small, therefore no heat uptake could be recorded in sections b–c of curve 3.

$$\text{sections a–b}\quad CuSO_4 \cdot 5H_2O^s \rightarrow (1-x)CuSO_4 \cdot 3H_2O^s + L_1^{sat}(= xCuSO_4 \cdot 3H_2O + 2H_2O^l) \cdots (+Q_1)$$

$$\text{sections b–c}\quad (1-x)CuSO_4 \cdot 3H_2O + L_1^{sat} \rightarrow (1-y)CuSO_4 \cdot 3H_2O^s + L_2^{sat}(= yCuSO_4 \cdot 3H_2O + 2H_2O^l) \cdots (+Q_2)$$

$$\text{sections c–d}\quad (1-y)CuSO_4 \cdot 3H_2O^s + L_2^{sat} \rightarrow CuSO_4 \cdot 3H_2O^s + 2H_2O^g \uparrow \cdots (+Q_3)$$

$$\text{sections e–f}\quad CuSO_4 \cdot 3H_2O^s \rightarrow CuSO_4 \cdot H_2O^s + 2H_2O^g \uparrow \cdots (+Q_4)$$

Between 97and 103 °C, as well as between 103 and 116 °C, the system absorbed an amount of heat corresponding to its heat capacity (Q_5, Q_6). This equals to the product of the average value of the molar heats (C_1, C_2) and the corresponding temperature range (T_2–T_1, T_4–T_3).

$$\text{sections b–c}\quad Q_5 = \bar{C}_1(T_2 - T_1)$$

$$\text{sections d–e}\quad Q_6 = \bar{C}_2(T_4 - T_3)$$

The amounts of heat proportional to the heat capacity of the samples, however, are usually so small that—as it is the case here—they cannot be observed on the Q-TA$_{T_s^n}$ curves, therefore—similarly to dissolution heats (Q_s)—they cannot be indicated. Therefore, for the sake of simplicity, further on they will be neglected.

Whereas on curve 3 in Fig. 2b the incongruent phase transformation can be shown unambiguously, there is no trace of such a process on the DTA curve in Fig. 2a. According to experience [1a], this process can only be recorded by a DTA investigation by using special experimental conditions.

4. Dehydration of $MnSO_4 \cdot 5H_2O$

Curves 3 and 4 in Fig. 3b illustrate the course of the dehydration of $MnSO_4 \cdot 5H_2O$ under “normal” conditions: as is seen the salt hydrate melted at 45 °C producing solid $MnSO_4 \cdot 4H_2O^s$ and a saturated solution (L_1^{sat}) (Fig. 3b, curve 3, sections a–b). At 75 °C, the $MnSO_4 \cdot 4H_2O$ decomposed further incongruently, and $MnSO_4 \cdot H_2O$ was formed, and the composition of the solution phase was changed (L_2^{sat}) (sections c–d). Then, the solution containing further only small amounts of the intermediate salt hydrate L_2^{sat} started to boil and evaporate at 103 °C. As the $MnSO_4{\cdot}H_2O^s$ intermediate precipitated from the L_2^{sat} solution in an amount proportional to the evaporating water vapour also in this case, the boiling point of the solution did not change until the temperature reached point f′.

As an end of evaporation, the remaining water left L_2^{sat} between points f′–f, whilst the temperature of the $MnSO_4{\cdot}H_2O^s$ and L_2^{sat} mixture being in a mass ratio of 20:1 increased from 103 to 270 °C. It can only be guessed why the temperature of the mixture should be elevated by nearly 170 °C for the water to leave the system (sections f′–f). At 270 °C, $MnSO_4{\cdot}H_2O^s$ decomposed to $MnSO_4{}^s$ and water vapour. This process was also anomalous. The process was introduced by nucleus formation. At the surface of the crystals, the number of nuclei is usually small. The temperature of the sample should be increased in order to reach the prescribed rate for the decomposition. At the point, however, when the number of nuclei is large enough, the temperature falls back spontaneously to the value required for the transformation to proceed under equilibrium conditions, with the rate prescribed. This process used to produce a beak-like formation on both the Q-TA$_{T_s^n}$ and Q-TG$_{T_s^n}$ curves [1b].

$$\begin{aligned}&\text{sections a–b}\quad MnSO_4\cdot 5H_2O^s\\&\quad\rightarrow (1-x)MnSO_4\cdot 4H_2O^s\\&\quad +L_1^{sat}(=xMnSO_4\cdot 4H_2O+H_2O^l)\cdots(+Q_1)\end{aligned}$$

$$\begin{aligned}&\text{sections c–d}\quad (1-x)MnSO_4\cdot 4H_2O^s+L_1^{sat}\\&\quad\rightarrow (1-y)MnSO_4\cdot H_2O^s\\&\quad +L_2^{sat}(=yMnSO_4\cdot H_2O^+ +4H_2O^l)\cdots(+Q_2)\end{aligned}$$

$$\begin{aligned}&\text{sections e–f}\quad (1-y)MnSO_4\cdot H_2O^s+L_2^{sat}\\&\quad\rightarrow MnSO_4\cdot H_2O^s+4H_2O^g\uparrow\cdots(+Q_3)\end{aligned}$$

$$\begin{aligned}&\text{sections f–g}\quad MnSO_4\cdot H_2O^s\\&\quad\rightarrow MnSO_4{}^s+H_2O\uparrow\cdots(+Q_4)\end{aligned}$$

5. Dehydration of $Mg(NO_3)_2{\cdot}6H_2O$

Curves 3 and 4 in Fig. 4b illustrate the course of water loss of $Mg(NO_3)_2{\cdot}6H_2O$ when this process is studied by the simultaneous Q-DTA, Q-TG method. According to curve $Q-TA_{T_s^n}$, the salt hydrate melted incongruently at 95 °C, and an unsaturated solution (L_1^{unsat}) appeared, and the simultaneously formed $Mg(NO_3)_2{\cdot}2H_2O$ immediately dissolved in it (sections a–b). The solution phase did not loose water till 150 °C (sections c–d), which fact could be proven from the Q-TG$_{T_s^n}$ curve.

The solution started to boil at 150 °C (point c). After that, the boiling point of the solution was continuously raised, as the system lost water, its concentration increased. This caused the inclined course of sections c–d of curves 3 and 4, which is an unambiguous sign for the solution being still unsaturated (L_2^{unsat}). A turn in this process occurred at point d of curves 3 and 4. Namely, the unsaturated solution at 280 °C became saturated ($L_2^{unsat}\rightarrow L_1^{sat}$). Following this, neither the boiling point of the solution, nor its concentration had further changed meaning that solid $Mg(NO_3)_2{\cdot}2H_2O$ precipitated from the solution in an amount proportional to the amount of water vapour leaving the system (sections d–e). This intermediate decomposed to $Mg(NO_3)_2{}^s$ and water vapour at

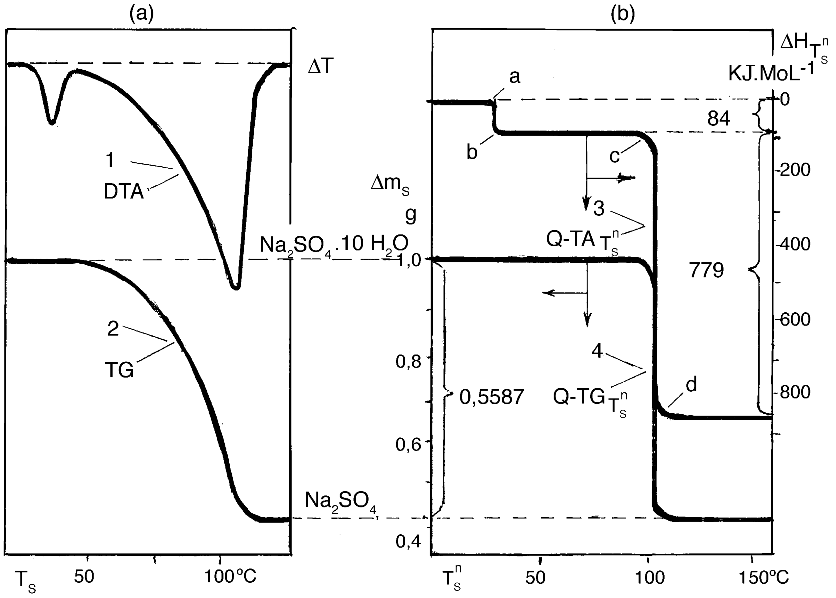

Fig. 5. Dehydration of $Na_2SO_4{\cdot}10H_2O$ studied by the traditional DTA, TG instrument (a) and by the simultaneous Q-DTA, Q-TG instrument (b).

390 °C (sections f–g).

$$\text{sections a–b}\quad Mg(NO_3)_2\cdot 6H_2O^s \rightarrow L_1^{unsat}(= Mg(NO_3)_2\cdot 2H_2O + 4H_2O^l)\cdots(+Q_1)$$

$$\text{sections c–d}\quad L_1^{unsat} \rightarrow L_2^{unsat}(= Mg(NO_3)_2\cdot 2H_2O + (4-x)H_2O^l) + xH_2O^g\uparrow\cdots(+Q_2)$$

$$\text{point d}\quad L_2^{unsat} \rightarrow L_1^{sat}$$

$$\text{sections d–e}\quad L_1^{sat} \rightarrow Mg(NO_3)_2\cdot 2H_2O^s + (4-x)H_2O^g\uparrow\cdots(+Q_3)$$

$$\text{sections f–g}\quad Mg(NO_3)_2\cdot 2H_2O^s \rightarrow Mg(NO_3)_2{}^s + 2H_2O^g\uparrow\cdots(+Q_4)$$

6. Dehydration of $Na_2SO_4{\cdot}10H_2O$

The dehydration of $Na_2SO_4{\cdot}10H_2O$ is, according to curves 3 and 4 in Fig. 5, a simple and unambiguous process. The salt hydrate melted incongruently at 32 °C, i.e. it decomposed to $Na_2SO_4{}^s$ and a solution L_1^{sat} (Fig. 5, curve 3, sections a–b). The solution L_1^{sat} of relatively low concentration started to boil at 104 °C, and without a change in temperature it evaporated totally (sections c–d). A sure sign of being this process isothermal was that the solution remained saturated.

$$\text{sections a–b}\quad Na_2SO_4\cdot 10H_2O^s \rightarrow (1-x)Na_2SO_4{}^s + L_1^{sat}(= Na_2SO_4{}^s + 10H_2O^l)\cdots(+Q_1)$$

$$\text{sections c–d}\quad (1-x)Na_2SO_4{}^s + L_1^{sat} \rightarrow Na_2SO_4{}^s + 10H_2O^g\uparrow\cdots(+Q_2)$$

7. Conclusions

On the traditional DTA, DSC curves, the course of physical and chemical transformations leading to equilibrium appears always deteriorated. Due to the open sample holder and the use of non-isothermal heating control, transformations proceed always in a non-isothermal way, in a more or less broad temperature range producing the deceptive appearance that they are not leading to equilibrium and they are irreversible (Figs. 2a–5a).

These problems are totally eliminated by using the "*simultaneous Q-DTA, Q-TG measuring technique*" (Figs. 2–5). Namely, the "*simultaneous Q-DTA, Q-TG instrument*" provides experimental conditions being near to the requirements of thermodynamics [12], thus processes free of foreign effects and leading to equilibrium proceed always strictly isothermally, and at a characteristic temperature being consequently the same and close to the theoretical value (Figs. 2b–5b).

However, isothermal transformations can be influenced by additionally proceeding foreign processes, but without changing the character of the reaction of leading to equilibrium [1c]. Such a process might be e.g. nucleus formation [1b] (Fig. 3b, curve 3, sections f–g), the delaying effect of a new solid phase on the leaving of the gaseous decomposition product [1d,6], modification of curves indicating the formation of intermediates [12], the evaporation of an unsaturated solution (Fig. 4, curve 3, sections c–d) [12], etc.

The irreversible transformations (decomposition of plastics, solid phase reactions, etc.) or the reversible but non-isothermal processes traceable to concentration changes in multicomponent systems [13], etc.) proceed always consequently non-isothermally, in the same temperature range with an unchanged course. Such processes are normalized by using the TGHC technique, but they are not influenced by the partial pressure of the gaseous decomposition products and the form of the sample holder.

On the traditional DTA, DSC curves, the course of transformations and their characteristic temperature change with the experimental conditions, therefore the value of transformation heat determined also changes (Kirchhoff's law). To the opposite, the course of Q-TA$_{T_s^n}$ curves and the characteristic temperature determined under normalized conditions do not change. The value of enthalpy changes read from these curves remain consequently constant [12] and reproducible.

The enthalpy changes of partial processes of complex reactions can also be read easily and with good accuracy from the Q-TA$_{T_s^n}$ curves (Figs. 2b–5b).

Though transformations proceed with a rate by orders of magnitude smaller by applying TGHC than in traditional DTA, DSC measurements using non-isothermal heating control, the total time for taking the curves by the new measuring technique increases only by a factor of two. Only the quasi-isothermal heating mode is time-consuming, as before and after the transformation the heating control may increase the temperature in a non-isothermal way, even by 20–30 °C min^{-1} [6,12,13]. The heating control switches from isothermal to non-isothermal heating mode and vice verse fully automatically.

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