

# Differential thermal analysis under quasi-isothermal, quasi-isobaric conditions (Q-DTA) Part IV. Latent error in the determination of the decomposition heat of salt hydrates decomposing congruently and incongruently

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## Abstract

The authors disclosed by the “*simultaneous Q-DTA, Q-TG*” method a latent, till now not known error in determining the decomposition heat of salt hydrates decomposing congruently or incongruently.

This error cannot be shown by the traditional calorimetric or thermoanalytical methods owing to overlapping of the processes taking part in the heat decomposition, it can only be detected and eliminated by applying the “*simultaneous Q-DTA, Q-TG*” method of very high resolution and selectivity.

A calculation technique is elaborated for the elimination of this error.

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*Keywords:* Simultaneous Q-DTA, Q-TG method; Transformation-governed heating control; Self-generated atmosphere; Decomposition heat of salt hydrates

## 1. Introduction

In a recent work, the authors studied the decomposition mechanism of several salt hydrates decomposing congruently or incongruently [1,2] by using their “*simultaneous Q-DTA, Q-TG*” method [3–6]. They established that in contrast to traditional DTA or DSC methods, by applying this measuring technique, the elementary processes of the complex transformations of salt hydrates can be fully separated, even if these processes overlap each other totally (Figs. 1–4).

In the course of their research work, the authors noted an error unknown until now, observable curiously enough mainly in the case of salt hydrates consisting of more elementary reactions and dissolving congruently, as well as in case of salt hydrates dissolving incongruently. In order to eliminate this error, a correction calculation method has been

elaborated. The present paper deals with the results of this research work.

## 2. Experimental conditions

The salt hydrates  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  have been studied earlier [2] for determining their heat decomposition mechanism. In the present paper, the objective was the determination of the decomposition heats of the same salt hydrates. Therefore, their stoichiometric composition (crystal water) was measured (Q-TG $T_3^n$  curve) very carefully, and the smaller deviations found were corrected by calculation.

Samples were studied by using the instrument Derivatograph C (Hungarian Optical Works, Budapest, system Paulik, Paulik, Erdely). This instrument was made applicable recently in addition for recording “*simultaneous TG, DTG, DTA, EGA*” [7] and “*quasi-isothermal, quasi-isobaric thermo-*

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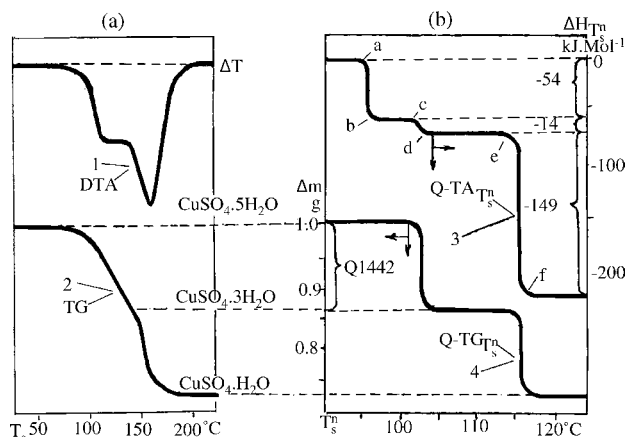


Fig. 1.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Curves recorded with the conventional DTA and TG (a) and simultaneous Q-DTA, Q-TG (b) methods: section a–b:  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}^s \rightarrow (1-x)\text{CuSO}_4 \cdot 3\text{H}_2\text{O}^s + \text{L}_1^{\text{sat}}$ ; section b–c:  $(1-x)\text{CuSO}_4 \cdot 3\text{H}_2\text{O}^s + \text{L}_1^{\text{sat}} \rightarrow (1-y)\text{CuSO}_4 \cdot 3\text{H}_2\text{O}^s + \text{L}_2^{\text{sat}}$ ; section c–d:  $(1-y)\text{CuSO}_4 \cdot 3\text{H}_2\text{O}^s + \text{L}_2^{\text{sat}} \rightarrow \text{CuSO}_4 \cdot 3\text{H}_2\text{O}^s \downarrow + 2\text{H}_2\text{O}^g \uparrow$ ; section e–f:  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}^s \rightarrow \text{CuSO}_4 \cdot \text{H}_2\text{O}^s + 2\text{H}_2\text{O}^g \uparrow$ .

gravimetry” (Q-TG) curves [7a,b], also for carrying out alternatively “simultaneous Q-DTA, Q-TG” [3–6] measurements, i.e. for taking  $\text{Q-TA}_{T_s^n}$  and  $\text{Q-TG}_{T_s^n}$  curves (Figs. 1b–4b), as well.

In Figs. 1a–4a traditional DTA and TG curves are shown. Figs. 1b–4b illustrate the course of the corrected enthalpy changes of samples (s) recorded in function of the temperature ( $T_s$ ) measured under normalized conditions (n) ( $\text{Q-TA}_{T_s^n}$ ) (curve 3), whereas the curve  $\text{Q-TG}_{T_s^n}$  (curve 4) shows the weight change of the sample. The results for enthalpy changes readable from curve 3 are also included in Tables 1–4 (column E).

On curve 3, as well as in the columns A of Tables 1–4, subsequent elementary processes of the transformations are indicated by sections a–b and c–d, etc. In columns B of

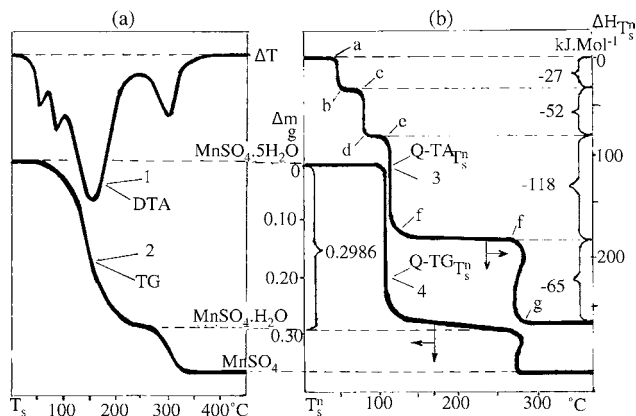


Fig. 2.  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ . Curves recorded with the conventional DTA and TG (a) and the simultaneous Q-DTA, Q-TG (b) methods: section a–b:  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}^s \rightarrow (1-x)\text{MnSO}_4 \cdot 4\text{H}_2\text{O}^s + \text{L}_1^{\text{sat}}$ ; section c–d:  $(1-x)\text{MnSO}_4 \cdot 4\text{H}_2\text{O}^s + \text{L}_1^{\text{sat}} \rightarrow (1-y)\text{MnSO}_4 \cdot 4\text{H}_2\text{O}^s + \text{L}_2^{\text{sat}}$ ; section e–f:  $(1-y)\text{MnSO}_4 \cdot 4\text{H}_2\text{O}^s + \text{L}_2^{\text{sat}} \rightarrow \text{MnSO}_4 \cdot 4\text{H}_2\text{O}^s \downarrow + 4\text{H}_2\text{O}^g \uparrow$ ; section f–g:  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}^s \rightarrow \text{MnSO}_4 \cdot \text{H}_2\text{O}^s + 3\text{H}_2\text{O}^g \uparrow$ .

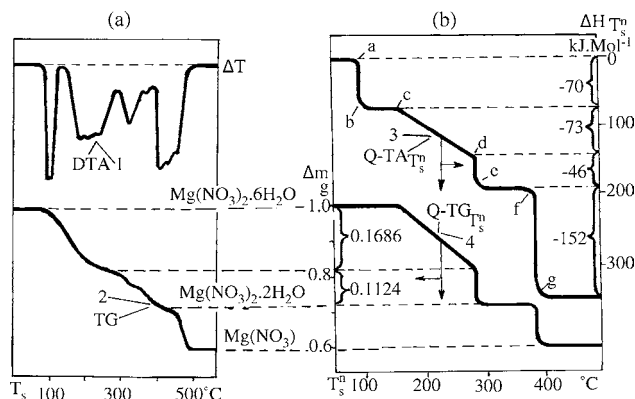


Fig. 3.  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . Curves recorded with the conventional DTA and TG (a) and the simultaneous Q-DTA, Q-TG (b) methods: section a–b:  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{L}_1^{\text{unsat}}$ ; section c–d:  $\text{L}_1^{\text{unsat}} \rightarrow \text{L}_2^{\text{unsat}} + x\text{H}_2\text{O}^g \uparrow$ ; point d:  $\text{L}_2^{\text{unsat}} \rightarrow \text{L}_1^{\text{sat}}$ ; section d–e:  $\text{L}_1^{\text{sat}} \rightarrow \text{Mg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}^s \downarrow + y\text{H}_2\text{O}^g \uparrow$ ; section f–g:  $\text{Mg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}^s \rightarrow \text{Mg}(\text{NO}_3)_2^s + 2\text{H}_2\text{O}^g \uparrow$ .

Tables 1–4, the reaction heats ( $\Delta^r H_{25^\circ\text{C}}^0$ ) calculated from the standard formation heats at  $25^\circ\text{C}$  ( $\Delta^f H_{25^\circ\text{C}}^0$ ), whereas in columns C and D the values of the enthalpy changes ( $\Delta H_{T_s^n}$ ) measured by the simultaneous Q-DTA, Q-TG instrument are shown. In columns E and F the corrected values are to be found.

The enthalpy change values measured directly by the Q-DTA, Q-TG instrument are obtained directly for 1 g of the sample in  $\text{kJ g}^{-1}$  (column C) which are then transformed into  $\text{kJ mol}^{-1}$  values (columns D), which is conform with the usual practice. For example, in different physico-chemical tables [8–10] the formation heats, transformation heats, molecular heats, etc. are given in  $\text{kJ mol}^{-1}$ . Therefore, the values for the salt hydrates obtained in  $\text{kJ g}^{-1}$  (column C) are all multiplied by the molecular mass ( $M_1$ ) of the compounds studied (columns D).

However, it turned out that we are only correct if the enthalpy change values of every elementary process (columns

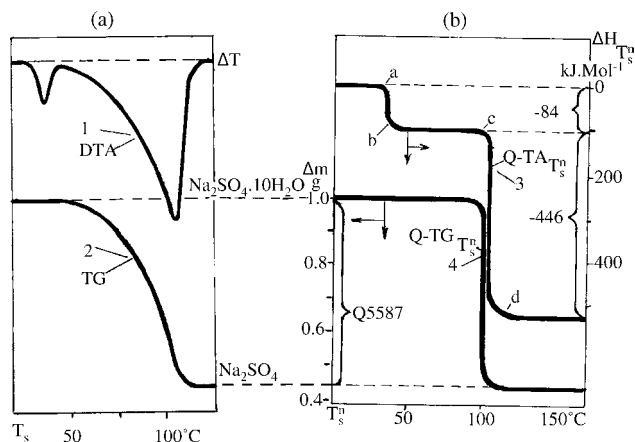


Fig. 4.  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . Curves recorded with the conventional DTA and TG (a) and the simultaneous Q-DTA, Q-TG (b) methods: section a–b:  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}^s \rightarrow (1-x)\text{Na}_2\text{SO}_4^s + \text{L}_1^{\text{sat}}$ ; section c–d:  $(1-x)\text{Na}_2\text{SO}_4^s + \text{L}_1^{\text{sat}} \rightarrow \text{Na}_2\text{SO}_4^s \downarrow + 10\text{H}_2\text{O}^g \uparrow$ .

Table 1  
CuSO<sub>4</sub>·5H<sub>2</sub>O

	A	B	C		D		E		F	
		$\Delta H_{25}^0$ Theoretical	$\Delta H_{T_s}^n$ Measured	Corrected (kJ Mol <sup>-1</sup> )						
		kJ Mol <sup>-1</sup>	kJ g <sup>-1</sup>	kJ Mol <sup>-1</sup>						
1	a-b		-0.215	-54	$M_1$	-54	$M_1$	-54	$M_1$	
2	c-d		-0.391	-98	$M_1$	-14	$M_2$	-13	$Q$	
3	e-f		-0.696	-174	$M_1$	-149	$M_3$	-149	$M_3$	
4	a-f	-227		-326		-217		-216		
5	Deviation of $\Delta H_{T_s}^n$ from $\Delta H_{25}^0$ in %			D - B + 44		E - B - 4		F - B - 5		

$M_1 = M_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}$ ,  $M_2 = M_{2\text{H}_2\text{O}}$ ,  $M_3 = M_{\text{CuSO}_4 \cdot 3\text{H}_2\text{O}}$ ,  $Q$  = evaporation heat:  $2.425 \text{ kJ g}^{-1} \times \text{weight of evaporated H}_2\text{O}$ :  $0.1442 \text{ g} \times M_{2\text{H}_2\text{O}}$ .

Table 2  
MnSO<sub>4</sub>·5H<sub>2</sub>O

	A	B	C		D		E		F	
		$\Delta H_{25}^0$ Theoretical	$\Delta H_{T_s}^n$ Measured	Corrected (kJ Mol <sup>-1</sup> )						
		kJ mol <sup>-1</sup>	kJ g <sup>-1</sup>	kJ mol <sup>-1</sup>						
1	a-b		-0.112	-27	$M_1$	-27	$M_1$	-27	$M_1$	
2	c-d		-0.235	-57	$M_1$	-52	$M_2$	-52	$M_2$	
3	e-f		-1.641	-396	$M_1$	-118	$M_3$	-52	$Q$	
4	g-h		-0.386	-93	$M_1$	-65	$M_4$	-65	$M_4$	
5	a-h	-278		-573		-262		-196		
6	Deviation of $\Delta H_{T_s}^n$ from $\Delta H_{25}^0$ in %			D - B + 106		E - B - 6		F - B - 29		

$M_1 = M_{\text{MnSO}_4 \cdot 5\text{H}_2\text{O}}$ ,  $M_2 = M_{\text{MnSO}_4 \cdot 4\text{H}_2\text{O}}$ ,  $M_3 = M_{4\text{H}_2\text{O}}$ ,  $M_4 = M_{\text{MnSO}_4 \cdot \text{H}_2\text{O}}$ ,  $Q$  = evaporation heat:  $2.425 \text{ kJ g}^{-1} \times \text{weight of evaporated H}_2\text{O}$ :  $0.2986 \text{ g} \times M_{4\text{H}_2\text{O}}$ .

Table 3  
Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O

	A	B	C		D		E		F	
		$\Delta H_{25}^0$ Theoretical	$\Delta H_{T_s}^n$ Measured	Corrected (kJ Mol <sup>-1</sup> )						
		kJ mol <sup>-1</sup>	kJ g <sup>-1</sup>	kJ mol <sup>-1</sup>						
1	a-b		-0.273	-70	$M_1$	-70	$M_1$	-70	$M_1$	
2	c-d		-1.012	-259	$M_1$	-73	$M_2$	-29	$Q_1$	
3	d-e		-0.645	-165	$M_1$	-46	$M_2$	-20	$Q_2$	
4	f-g		-0.825	-212	$M_1$	-152	$M_3$	-152	$M_3$	
5	a-g	-370		-706		-341		-271		
6	Deviation of $\Delta H_{T_s}^n$ from $\Delta H_{25}^0$ in %			D - B + 91		E - B - 8		F - B - 27		

$M_1 = M_{\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}}$ ,  $M_2 = M_{4\text{H}_2\text{O}}$ ,  $M_3 = M_{\text{Mg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}}$ ,  $Q_1/Q_2$  = evaporation heat:  $2.425 \text{ kJ g}^{-1} \times \text{weight of evaporated water}$ :  $0.1686/0.1124 \text{ g} \times M_{4\text{H}_2\text{O}}$ .

Table 4  
Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O

	A	B	C		D		E		F	
		$\Delta H_{25}^0$ Theoretical	$\Delta H_{T_s}^n$ Measured	Corrected (kJ Mol <sup>-1</sup> )						
		kJ mol <sup>-1</sup>	kJ g <sup>-1</sup>	kJ mol <sup>-1</sup>						
1	a-b		-0.262	-84	$M_2$	-84	$M_1$	-84	$M_1$	
2	c-d		-2.479	-799	$M_1$	-446	$M_2$	-244	$Q$	
3	a-d	-521		-883		-530		-328		
4	Deviation of $\Delta H_{T_s}^n$ from $\Delta H_{25}^0$ in %			D - B + 70		E - B + 2		F - B - 37		

$M_1 = M_{\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}}$ ,  $M_2 = M_{10\text{H}_2\text{O}}$ ,  $Q$  = evaporation heat:  $2.425 \text{ kJ g}^{-1} \times \text{weight of evaporated water}$ :  $0.5587 \text{ g} \times M_{10\text{H}_2\text{O}}$ .

C) are multiplied with the molecular mass ( $M_1, M_2, M_3 \dots$ ) of the respective starting compound, or if the corrected results of the measurement (columns E) are recorded as functions of them (Figs. 1b–4b, curves 3).

Thus, taking  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as an example, in the elementary reaction a–b,  $M_1 = M_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}$ , in reaction c–d,  $M_2 = 2 \times M_{\text{H}_2\text{O}}$ , in e–f,  $M_3 = M_{\text{CuSO}_4 \cdot 3\text{H}_2\text{O}}$  molecular masses should be taken as multiplication factors. In the case of the evaporation of the solution phase, the number of water molecules leaving the system has also to be taken into account.

In order to prove the correctness of this calculation method, it was also calculated what amount of heat ( $Q$ ) was needed for the evaporation of the liquid water liberated in the process (c–d). Therefore, by taking again  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as an example, the amount of evaporated water was read from the Q-TG curve (Fig. 1b, curve 4) ( $\Delta m = 0.1442 \text{ g}$ ) and this was multiplied by the evaporation heat of water ( $2.425 \text{ kJ g}^{-1}$ ), by the molecular mass of water, and by the number of water molecules evaporated ( $2 \times M_{\text{H}_2\text{O}}$ ) (Table 1, column F, line 2).

The correctness of the above calculation is supported also by comparing the measured (column D) and the corrected enthalpy change values (columns E and F) with the one calculated from the standard formation heats of the reaction partners resulting in standard reaction heats which can be considered a theoretical value (column B) ( $\Delta^r H_{25^\circ\text{C}}^0$ ). The percentual differences between theoretical, measured and corrected values (D–B, E–B, F–B) are given in the last lines (lines 4–6) of Tables 1–4.

The value of the reaction heat changes with the temperature (Kirchoff's law). Therefore, the question may arise what error is made if we compare the measured and corrected enthalpy changes ( $\Delta H_{T_s}^n$ ) of partial reactions taking place at temperatures different ( $T_s$ ) from ambient ( $25^\circ\text{C}$ ) temperature (Tables 1–4, columns D, E and F) with the standard reaction heats valid at  $25^\circ\text{C}$  ( $\Delta^r H_{25^\circ\text{C}}^0$ ) (columns B). The newer physico-chemical tables [8–10] contain also the changes of formation heats with temperature. Thus, the values of standard reaction heats were recalculated to the characteristic temperatures of the elementary reactions, and this was compared with the similarly recalculated measured and corrected values of the reaction heats for the elementary reactions. The differences determined by these types of calculations were found so small that they did not modified essentially the latent error. Therefore, such kinds of corrections were neglected in later calculations.

### 3. Discussion

#### 3.1. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

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

According to publications cited in the References without striving for completeness [7c,11–18], many questions arose

earlier concerning the interpretability of traditional DTA and DSC curves. Unambiguous answers are given to these questions by the curves of Fig. 1b.

At  $96^\circ\text{C}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was melted in its own crystal water, and the solution contained solid  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}^s$  and a saturated solution containing trihydrate (Fig. 1b, curve 3, section a–b). At  $103^\circ\text{C}$ , the solution started to boil, then it evaporated isothermally (section c–d). Before reaching the boiling point, the weight of the sample remained strictly constant (curve Q-TG $_{T_s}^n$ ). The solid  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}^s$  remnant decomposed at  $116^\circ\text{C}$  to solid  $\text{CuSO}_4 \cdot \text{H}_2\text{O}^s$  and water vapour (section e–f).

##### 3.1.2. Determination of the decomposition heat of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

In section a–d of curve 3 in Fig. 1b ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ ) an enthalpy change of  $-152 \text{ kJ mol}^{-1}$ , whereas in section d–f ( $\text{CuSO}_4 \cdot 3\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot \text{H}_2\text{O}$ ) that of  $-174 \text{ kJ mol}^{-1}$  was measured by the authors (Table 1, column D, lines 1–3). In order to check the values measured, the authors looked for earlier data but no reliable data could be found in the literature.

##### 3.1.3. Earlier results

At the beginning (1910–1960), the decomposition heat of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was determined mainly by calorimetric measurements (dehydration and rehydration heats, dissolution heat, etc.) and by determining the change in vapour pressure [19]. The most probable values seemed to be, among many different ones for both transformations, for  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot 3\text{H}_2\text{O} -249 \text{ kJ mol}^{-1}$ , and for  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot \text{H}_2\text{O} -249 \text{ kJ mol}^{-1}$ , respectively [20].

In the fifties, Kissinger [21], by publishing his equation derived from the Arrhenius relationship brought into fashion to apply reaction kinetic parameter calculations. The famous experiment of Borhardt and Daniels [22] seemed to justify the findings of Kissinger. After that, thermo-analytical experts determined the transformation heats of every compound, also the dehydration heat of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  [23–28] almost exclusively [29] by calculating reaction kinetic parameters, in spite of the fact that the results scattered between  $-180$  and  $-360 \text{ kJ mol}^{-1}$  for the reaction  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot \text{H}_2\text{O}$ .

This had remained alive almost up to now, in spite of the fact that it turned out already at the beginning that the parameter calculation is unsuitable for determining reaction heats.

Attention to this fact was called, e.g. by the inventors of the Q-TG method as soon as in 1971 [30]. Later on, they and their coworkers supported this criticism also by practical examples [7d,31–34].

According to their opinion, the Arrhenius relationship cannot be criticized in its own place, but it is not applicable for determining the activation enthalpy of reactions leading to equilibrium by using a non-isothermal heating program and

open sample holder for taking the DTA, DSC and TG curves being the basis for parameter calculation.

It is namely well-known that the traditional experimental conditions are capable of modifying the course of curves TG, DTA and DSC to such an extent that they are characteristic rather for the experimental conditions and not for the reaction itself [7e].

### 3.1.4. Determination of the reaction heat of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ by the “simultaneous Q-DTA, Q-TG method”

As the authors did not find reliable comparative data in the literature, they calculated the sums of standard reaction heat ( $\Delta^r H_{25^\circ\text{C}}^0$ ) of the two-step decomposition process, of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  from the standard formation heats ( $\Delta^f H_{25^\circ\text{C}}^0$ ) of the reaction partners formed [8–10] according to thermochemical rules (Table 1, column B, line 4). This was then compared with the enthalpy change measured (column D, line 4, Fig. 1b, curve 3). A difference of 44% has been found between the measured and the theoretical values (columns D–B, line 5).

In order to disclose the reason for this deviation, the dehydration heats of other salt hydrates ( $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) were also determined, and even bigger differences (+70, +91, +106) were found between the theoretical and measured values (columns D–B). Curiously, these unprobably big deviations helped to find the reason for a latent, till now unknown error.

It turned out, namely, that the error was caused by the fact that the authors calculated the enthalpy values of the elementary reactions measured in  $\text{kJ g}^{-1}$ , e.g. for the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in the traditional way, by multiplying it with the molecular mass ( $M_1$ ) of the original compound ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) into the dimension of  $\text{kJ mol}^{-1}$  (column D).

It also turned out that it would have been correct to handle the elementary processes of the dehydration of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (section a–b, etc.) as independent processes from the viewpoint of the calculations, and the enthalpy values obtained in the dimension of  $\text{kJ g}^{-1}$  (Table 1, column C) should have been multiplied by the molecular masses of the respective starting compounds ( $M_1$ ,  $M_2$ ,  $M_3$ ) and by the number of the participating molecules, which are in case of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ :  $M_1 = M_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}$ ,  $M_2 = 2 \times M_{\text{H}_2\text{O}}$ ,  $M_3 = M_3 = M_{\text{CuSO}_4 \cdot 3\text{H}_2\text{O}}$ . The results are obtained in this case in  $\text{kJ mol}^{-1}$ , but in a corrected value (column E, lines 1–3). The sum of the reaction heats thus corrected (column E, line 4) shows a difference of only –4% (columns E–B, line 5) when compared with the theoretical value.

Though the satisfactory agreement has a supporting value, another way was also found to control the correctness of the calculation method. It was calculated, e.g. what amount of heat ( $Q$ ) was taken up, later during the evaporation of the saturated solution (section c–d). The weight of the water evaporated according to curve Q-TG $_{T_s}^n$  was multiplied by the evaporation heat of water, by the molecular mass of water and by the number of molecules taking part in section c–d. The

result of this calculation (–5%) (column F, line 5) hardly differs from the values measured and corrected (column E, line 5) what makes also probable that the correction calculation is right.

The dehydration heats of other salt hydrates having different decomposition mechanisms than that of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  have also been measured by the “simultaneous Q-DTA, Q-TG” method. In these cases the latent error was even bigger.

### 3.2. $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$

According to the curves Q-TA $_{T_s}^n$  and Q-TG $_{T_s}^n$  in Fig. 2b,  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$  was melted incongruently in its own crystal water at 35 °C by forming solid  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}^s$  and a saturated solution ( $L_1^{\text{sat}}$ ) (curve 3, section a–b). At 55 °C,  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  also decomposed, and an intermediate,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}^s$  and also a saturated solution of the monohydrate ( $L_2^{\text{sat}}$ ) was formed (section c–d). The later saturated solution started to boil at 102 °C, then it evaporated isothermally. In the same time, the dissolved  $\text{MnSO}_4 \cdot \text{H}_2\text{O}^s$  proportional to the evaporating water, precipitated. At 270 °C, the remaining  $\text{MnSO}_4 \cdot \text{H}_2\text{O}^s$  decomposed to  $\text{MnSO}_4^s$  and water vapour. This process was originally also isothermal, but due to a delayed nucleus formation, the temperature of the monohydrate increased temporarily to 275 °C (section f–g). According to experience [1,2,7f], the beak-like course of curve 3 and is a sign for delayed nucleus formation.

The f–f section of the Q-TA $_{T_s}^n$  and Q-TG $_{T_s}^n$  curves is also worth of attention. This indicates that in this temperature range the sample took up a small amount of heat by losing at the same time a little weight. Between 100 and 270 °C the concentration of the residual solution increased again, because the solubility of the monohydrate increased rapidly with rising temperature. It can be supposed that towards the end of evaporation, from the large amount of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}^s$ , microcrystals precipitated, and from the syrup-like, concentrated solution a mush-like pulp was formed, at the surface of which a crust could be developed [7g] which hindered the removal of the last remnants of water.

In case of the  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ , there is a big difference (+106%) (line 6, columns D–B) between the theoretical (column B, line 5) and the measured and traditionally calculated (column D, line 5) values. This big difference could be decreased to –6% (columns E–B, line 6) by the correction calculation proposed (column E). The difference between the theoretical and corrected enthalpy changes (columns F–B, line 6), however, increased to –29% when the evaporation heat of pure water was used instead of that of the saturated solution measured in calculating the absorbed amount of heat ( $Q$ ). This later way of calculation is only an approaching one because it let out of consideration that between 50 and 250 °C further different kind of exothermal and endothermal elementary processes (e.g. change of heat capacity) took place. Due to this can be explained the difference between the two corrected values (–6 and –29%).



### 3.3. $Mg(NO_3)_2 \cdot 6H_2O$

Following information can be read from curves  $Q-TA_{T_s^n}$  and  $Q-TG_{T_s^n}$  in Fig. 3.

$Mg(NO_3)_2 \cdot 6H_2O$  melted congruently at 90 °C in its own crystal water (section a–b), and an unsaturated solution was formed (section b–c), which started to boil at 130 °C. From the boiling solution water vapour was evaporated (curve  $Q-TG_{T_s^n}$ ), and at the same time, both the boiling temperature and, to a proportional extent, the concentration of the solution increased continuously (section c–d). The solution became saturated at 280 °C. From then on, parallelly, water vapour left the solution (curve  $Q-TG_{T_s^n}$ ), and in a proportional amount, solid  $Mg(NO_3)_2 \cdot 2H_2O^s$  precipitated at a constant temperature. The water loss of an unsaturated solution is always non-isothermal, whereas that of saturated solutions is isothermal [1,2]. The dihydrate decomposed at 370 °C to  $Mg(NO_3)_2^s$  and water vapour.

Table 3 also proves that in calculating the enthalpy changes, the above described correction calculation should be applied. Without this correction, namely, the error would have been also in this case very large, +91% (columns D–B, line 5), whereas the difference with using the corrected enthalpy change makes only –8% (columns E–B).

### 3.4. $Na_2SO_4 \cdot 10H_2O$

Dehydration of  $Na_2SO_4 \cdot 10H_2O$  is a simple, well interpretable process.

According to curve 3 in Fig. 4b, the salt hydrate melted in its own crystal water at 32 °C, and water-free  $Na_2SO_4^s$  and a saturated solution were formed. The latter evaporated at 104 °C with boiling without any temperature change forming precipitated  $Na_2SO_4^s$ .

As Table 4 shows, a difference between the theoretical and measured enthalpy change values of +70% found (columns D–B, line 4), whereas in case of the corrected and non-corrected values this difference was only +2% (columns E–B, line 4) and –37% (columns F–B, line 4), respectively.

## 4. Conclusions

- (1) The course of traditional DTA, DSC, TG, EGA, etc. curves is the resultant of partly the enthalpy and weight changes accompanying the chemical and physical transformations, and partly are influenced by the effects of additional elementary processes modifying their course (e.g. nucleus formation), as well as by the effects of material- and heat-transport, which are, however, out of our interest. The latter effects are also functions of the experimental conditions, but sometimes they modify the course of the curves to such an extent that they are characteristic for material- and heat-transport processes rather than for the transformation studied.
- (2) This deteriorating effect of material- and heat-transport processes are totally eliminated by using the “*simultaneous Q-DTA, Q-TG measuring technique*”. The explanation for this is that the experiment is carried out under optimum experimental conditions which are not equal, but very near to those required by thermodynamics determined by theoretical considerations. This approximation of the ideal conditions is made possible by the use of the “*labyrinth crucible*” instead of traditional open sample holders and the “*transformation-governed heating control*” instead of a non-isothermal heating program. The former generates in its inside a pure, “*self-generated atmosphere*” of 100 kPa pressure, whereas the latter, on a feed-back principle, regulates the sample temperature so that the difference in the temperature between the sample and the reference material ( $\Delta T$ ) is always such that the transformation takes place with a constant rate being by orders of magnitude smaller than the traditional one ( $dH_t/dt \sim dm/dt$ ). The result:
- (3) By applying the “*simultaneous Q-DTA, Q-TG method*”:
  - (3a) Transformations leading to equilibrium and free of every additional elementary processes or other effects take place always in a strictly isothermal way at a temperature characteristic for the transformation (Figs. 1b–4b).
  - (3b) The course of equilibrium transformations is modified to non-isothermal on sections of the process where some foreign effect leading also to equilibrium appears (e.g. change of the boiling point in multicomponent systems with changing composition (Fig. 3b, curves 3 and 4, section c–d) or change in the melting point [7], or in cases where additional elementary processes of non-equilibrium nature (e.g. nucleus formation) take also place (Fig. 2b, curves 3 and 4, section f–g), or an increase of the crust thickness of the newly formed phase hindering the free removal of the gaseous decomposition products plays a role (Fig. 2b, curves 3 and 4, section f–f)).
  - (3c) Reactions not leading to equilibrium (e.g. thermal decomposition of organic compounds) run in a non-isothermal way. The repetition of the studies provides ( $Q-TA_{T_s^n}$  and  $Q-TG_{T_s^n}$  curves of unchanged course characteristic for the given compound. In these cases, the course of thermal decomposition is independent of the partial pressure of the gaseous decomposition product. Use of a labyrinth crucible or inert gas is advisable, but only for protecting the sample from the oxidative effect of air.
- (4) To the contrary of using traditional methods, the extraordinary resolution capability and selectivity of the simultaneous Q-DTA, Q-TG method allow to separate the subsequent elementary processes in simple and complex systems, and to identify them by their characteristic course, as well as to determine their enthalpy and weight changes separately.

- (5) The large resolution and selectivity of the simultaneous Q-DTA, Q-TG method made possible to discover a latent, till now unknown hidden mistake in the static (calorimetric) and dynamic (DTA, DDC, DSC) determination of the enthalpy changes in complex transformations leading to equilibrium. Until now, it was usual to multiply the results obtained in  $\text{kJ g}^{-1}$  dimension by the molecular mass of the starting material, obtaining thus the result in  $\text{kJ mol}^{-1}$  as given in, e.g. physico-chemical tables. However, the right way is to consider the partial processes as series of individual processes, and the results obtained in  $\text{kJ g}^{-1}$  are multiplied by the molecular mass of the starting materials of the partial process, and then, by summing them up, we obtain the end result in  $\text{kJ mol}^{-1}$ .

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