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DEPENDENCE OF THE THERMAL DECOMPOSITION OF $CuSO_4 \cdot 5H_2O$ ON THE EXPERIMENTAL CONDITIONS

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The mechanism of thermal decomposition of $CuSO_4 \cdot 5H_2O$ is greatly influenced by the experimental conditions. Under conventional conditions, in an open crucible, the first partial reaction takes place in one step involving solid and gaseous phases. If a sample holder which creates a self-generated atmosphere is used, the reaction is separated into two consecutive processes. First the sample melts in an incongruent way, and thereafter the saturated solution formed beside solid $CuSO_4 \cdot 3H_2O$ evaporates under boiling. These two processes can be completely distinguished in the DTA curve. The selectivity of the examinations can be further increased through application of the quasi-isothermal heating technique.

The two modes of decomposition can be correlated with the special phenomenon that, if the decomposition occurred according to the former mechanism, then the intermediate $CuSO_4 \cdot 3H_2O$ had stoichiometric composition, while in the latter case the compound consequently contained about 2.5% more water than that calculated.

One of the aims of thermoanalytical investigations is to acquire a better knowledge of the mechanisms of transformations which take place in various compounds in response to heat. With the rapid development of thermal analysis, more and better possibilities present themselves for the achievement of this aim. In the past few decades, the development of new measuring techniques and the improvement of the devices have increased the resolution and selectivity of the examinations to such an extent that, with not too much exaggeration, one could even say that every compound that has already been examined and considered to be known, could be examined again. Such control examinations do not generally change our earlier knowledge regarding a given compound fundamentally. However, the possibility of observing new quantitative correlations, of finding

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more exact characteristic temperatures or of detecting previously unknown partial processes of transformations may considerably broaden our earlier knowledge.

An example connected with the dehydration of $CuSO_4 \cdot 5H_2O$ is shown in the present work.

Experimental

Apparatus

The examinations were carried out by means of the latest, computer-controlled type of the derivatograph (derivatograph–C, produced by the Hungarian Optical Works, Budapest) [1, 2].

The accessories of this device include two, earlier developed sample holders [3, 4], inside which a "self-generated" atmosphere can be established. One of these sample holders is called a labyrinth crucible (Fig. 1/1), while the other is called a conial crucible (Fig. 1/2).

The labyrinth crucible consists of three crucibles and of three covering parts that slide into one another. In the closed state, the walls of these parts fit tightly into one another. When the material situated in the innermost crucible begins to decompose, the liberated gaseous products expel the air from the inside of the crucible and their partial pressure increases to 100 kPa, which stays constant (isobaric) until the end of the transformation.

A similar effect can be achieved with the conical crucible (Fig. 1/2). The lower part of this is a crucible, which is similar to the superficies of a truncated cone. Into its wall, a screw-thread-like cavity is cut. When the covering part is put upon the crucible, this cavity forms a spiral-like tight channel. By streaming outwards through this channel, the decomposition products prevent air from streaming into the crucible from the opposite direction. In this case too, a "self-generated" atmosphere is established within the crucible.

This circumstance greatly influences the performance of the reactions, even if the conventional linear heating pogramme is applied, as shown in Figs 2/i–m. The simultaneous TG, DTG and DTA curves in these Figures were traced by using the conical crucible. For the sake of comparison, examinations under conventional conditions were also performed with an open (Figs 2/a–d) and with a covered crucible (Figs 2/e–h). The heating rate was changed from 0.1 to 1, 2 and 4 deg min^{-1} in the sequence of Figs a–d, e–h and i–m, respectively. The amount of sample in every case was ca. 170 mg.

However, curves with quite a different course can be obtained if the advantages of the quasi-isothermal heating technique [3–6] are added to the advantages of the

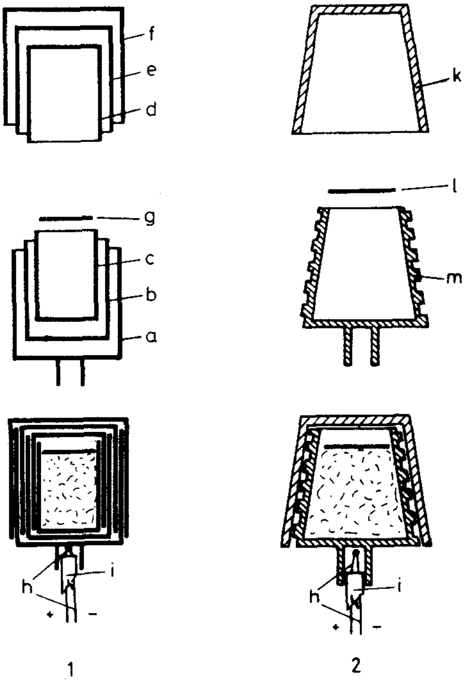


Fig. 1 Labyrinth (1) and conic (2) crucibles. a, b, c under and d, e, f upper parts of the labyrinth crucible, g, l platinum sheet, h thermocouple, i corundum tube, m under and k upper parts of the conic crucible

"self-generated" atmosphere. As a consequence of the condition that the decomposition occurs at a strictly constant rate, lower by several orders of magnitude than the conventional decomposition rate, the reactions leading to equilibrium take place without any temperature change (quasi-isothermal). Due to this, the partial processes of the transformation become separated and the selectivity and resolution of the examination increase, as can be seen in Figs 3 and 4.

The Q–TG curves 1, 2, 3, 5 and 6 in Fig. 3 demonstrate the first and second steps of the process of dehydration of $CuSO_4 \cdot 5H_2O$ as a function of temperature. In order to detect the influence of the shape of the sample holder, various types of holders were applied: multi-plate sample holder (curve 1), open crucible (curve 2), covered crucible (curve 3), conical crucible (curves 4 and 5) and labyrinth crucible (curve 6). The weight of the sample was ca. 340 mg and the rate of the transformation was 0.5 mg min^{-1} ($\Sigma \Delta m = 100$ mg H_2O). In the case of curve 4, the test material was 50 mg water.

Figure 4 shows the original diagrams traced as a function of time, on the basis of

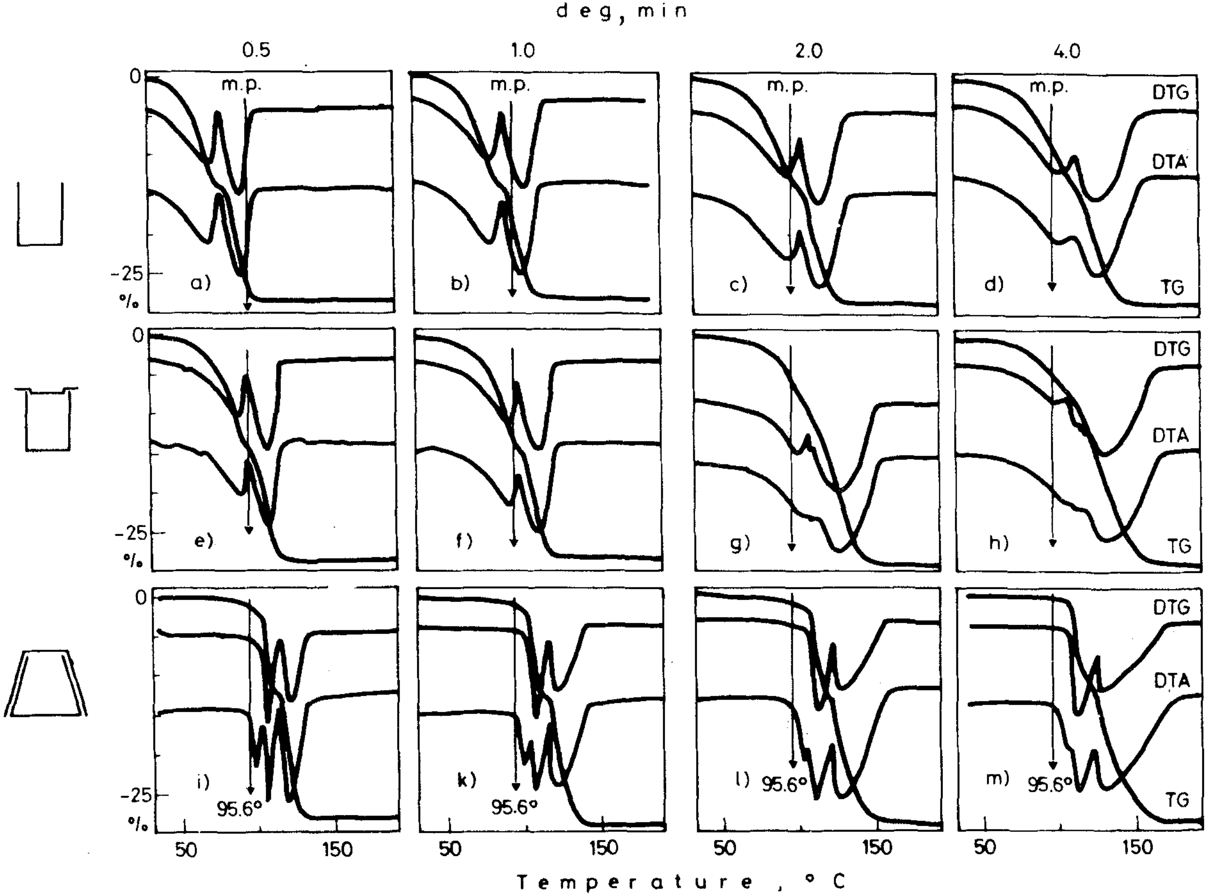


Fig. 2 Original diagrams of the dehydration of $CuSO_4 \cdot 5H_2O$. Measuring technique: conventional simultaneous TG, DTG and DTA. Crucibles: open (curves a–d), covered (curves e–h) and conic (curves i–m). Heating rate: 0.5 deg min^{-1}, $\Sigma\Delta m = 100$ mg (curves a, e, i), 1 deg min^{-1} (curves b, f, k), 2 deg min^{-1} (curves c, g, l) and 4 deg min^{-1} (curves d, h, m). Sample weight: 170 mg

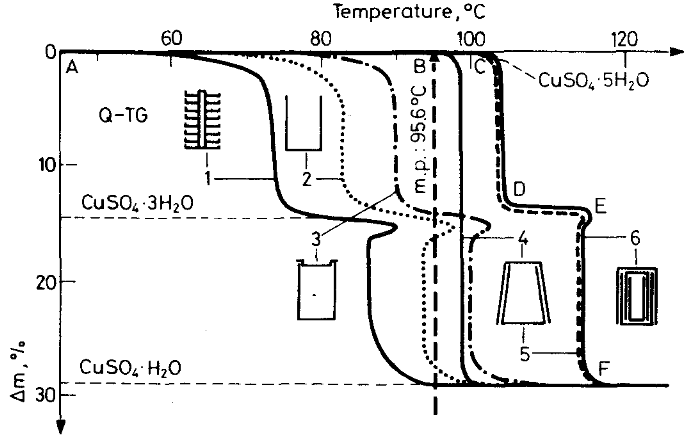


Fig. 3 Q–TG curves of the dehydration of $CuSO_4 \cdot 5H_2O$ (curves 1, 2, 3, 5, 6) and boiling of pure water (curve 4). Measuring technique: Simultaneous Q–TG, Q–DTG and Q–DTA technique. Sample holder: multi plate (curve 1) sample holder, open (curve 2), covered (curve 3), conic (curves 4, 5) and labyrinth crucibles (curve 6). Transformation rate: 0.5 mg min^{-1}, $\Sigma\Delta m$ = 100 mg. Weight of $CuSO_4 \cdot 5H_2O$: 340 mg (curves 1, 2, 3, 5, 6). Weight of the water: 50 mg (curve 4). Curves 3, 4, 5 and 6 are identical with the TG curves of Fig. 4/a, b, d and c

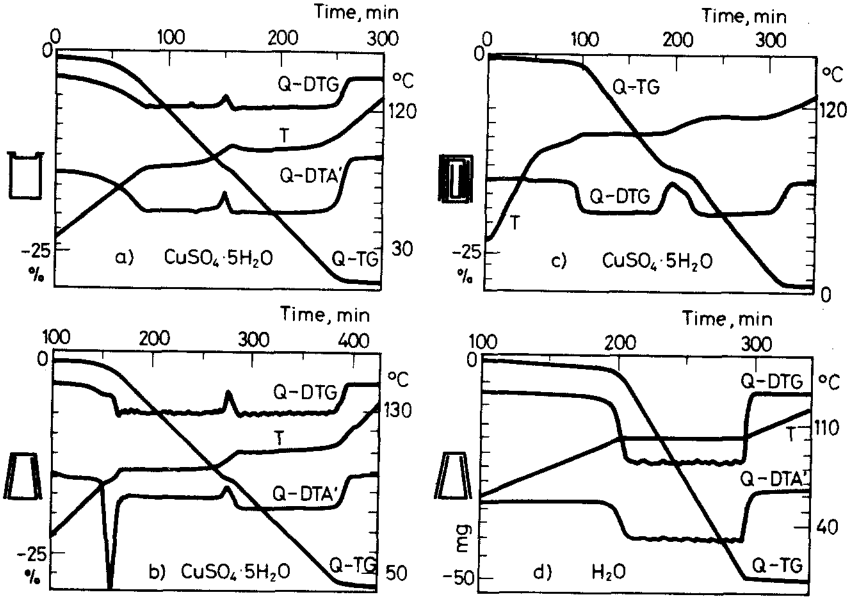


Fig. 4 Original diagrams of the dehydration of $CuSO_4 \cdot 5H_2O$ (Fig. 4/a, b and c) and of boiling of water (Fig. 4/d). Measuring technique: Simultaneous Q–TG, Q–DTA and DTG technique. Crucibles: covered (curve a), conic (curves b, d) and labyrinth (curve c). Transformation rate: 0.5 mg min^{-1}, $\Sigma\Delta m$ = 100 mg. Weight of $CuSO_4 \cdot 5H_2O$: 340 mg (curves a–c). Weight of the water: 50 mg (curve d). Curves in Fig. 4/a, b, c and d are identical with curves 3, 5, 6, and 4 of Fig. 3

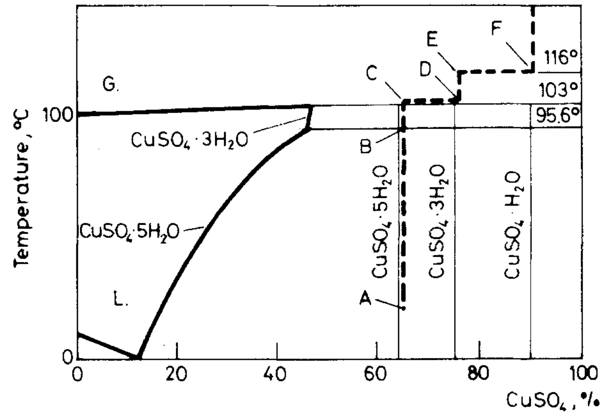


Fig. 5 Phase diagram of $CuSO_4 \cdot 5H_2O$ system. Path of the transformation: curve A–F. This is identical with curve 6 in Fig. 3 but illustrated in another coordinate system

which curve 3 (diagram *a*), curve 4 (diagram *d*), curve 5 (diagram *b*) and curve 6 (diagram *c*) of Fig. 3 were redrawn as a function of temperature.

Figure 5 demonstrates schematically the phase diagram of the $CuSO_4$–H_2O system. Here, the dotted line marks the path (A–F) along which the dehydration took place under the same experimental conditions as applied to trace curve 6 in Fig. 3. Essentially, both curves demonstrate the very same changes in the corresponding values of the relation temperature *vs.* composition, but in two different kinds of coordination system.

If the labyrinth or conical crucibles were applied, it was observed that the amount of water released was 2.5% less in the first period of the decomposition and about 2.5% more in the second, computed on the total theoretical amount of water of crystallization. This phenomenon, which initially seemed to be a measurement error, was studied systematically.

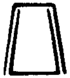
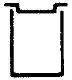
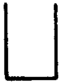
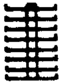
Table 1 contains the results of 11 parallel measurements carried out by using the quasi-isothermal measuring technique and the labyrinth crucible under the same conditions as were applied to trace curve 6 in Fig. 3.

This series of measurements was repeated under the same experimental conditions with a conical (curve 5 in Fig. 3), a covered (curve 3) and an uncovered (curve 2) crucible, and with the multi-plate sample holder (curve 1). The mean values of the results of these parallel measurements and the deviations of the mean values from the theoretical value are given in Table 2.

Table 1 Determination of the water released in the course of the decomposition of $CuSO_4 \cdot 5H_2O$. Means of 11 parallel measurments. Measuring technique: quasi-isothermal. Sample holder: labyrinth crucible. Transformation rate: 0.5 mg min^{-1}. $\Sigma \Delta m$ = 100 mg. Weight of sample: 340 mg

		Step I	Deviation		Step II	Deviation		Step III	Deviation		Steps I+II+III	Deviation		
Theor. values		40.00			40.00			20.00			100.0			%
Measured values	1	37.69	−0.02	−2.31	42.04	−0.50	+2.04	20.02	−0.11	+0.02	99.75	−0.63	−0.25	%
	2	37.32	−0.39	−2.68	42.82	+0.28	+2.82	19.96	−0.17	−0.04	100.10	−0.28	+0.10	%
	3	37.90	+0.19	−2.10	42.58	+0.04	+2.58	20.35	+0.22	+0.35	100.83	+0.45	+0.83	%
	4	37.26	−0.45	−2.74	42.62	+0.08	+2.62	19.98	−0.15	−0.02	99.86	−0.52	−0.14	%
	5	37.48	−0.23	−2.52	42.35	−0.19	+2.35	20.66	+0.53	+0.66	100.49	+0.11	+0.49	%
	6	37.21	−0.50	−2.79	42.27	−0.27	+2.27	20.22	−0.09	+0.22	99.70	−0.68	−0.30	%
	7	38.23	+0.52	−1.77	42.33	−0.21	+2.33	20.21	+0.08	+0.21	100.77	+0.39	+0.77	%
	8	38.04	+0.33	−1.96	43.05	+0.51	+3.05	19.87	−0.26	−0.13	100.96	+0.58	+0.96	%
	9	37.78	−0.07	−2.22	42.52	−0.02	+2.52	20.13	+0.00	+0.13	100.43	+0.05	+0.43	%
	10	38.25	+0.54	−1.75	42.24	−0.30	+2.24	19.92	−0.21	−0.08	100.41	+0.03	+0.41	%
	11	37.67	−0.04	−2.33	43.07	+0.53	+3.07	20.16	+0.03	+0.16	100.90	+0.52	+0.90	%
Mean values		37.71			42.54			20.13			100.38			
Deviation from mean values			±0.30			±0.27			±0.17			±0.39		
Deviation from theor. values				−2.29			+2.54			+0.13			+0.38	

Table 2 Determination of water released in the course of the decomposition of $CuSO_4 \cdot 5H_2O$. Means of 11 parallel measurements. Measuring technique: quasi-isothermal heating. Different kinds of sample holder. Transformation rate: 0.5 mg min^{-1}. $\Sigma \Delta m$ = 100 mg. Weight of sample: 340 mg

		Step I		Step II		Step III		Steps I+II+III		
		Mean values	Deviation from theor. value	Mean values	Deviation from theor. value	Mean values	Deviation from theor. value	Mean values	Deviation from theor. value	
Theoretical values		40.00		40.00		20.00		100.0		%
Sample holders										
	labyrinth	37.7	−2.3	42.5	+2.5	20.2	+0.2	100.4	+0.4	%
	conical	37.8	−2.2	42.4	+2.4	19.9	−0.1	100.1	+0.1	%
	covered	40.2	+0.2	40.1	+0.1	19.8	−0.2	100.1	+0.1	%
	open	40.1	+0.1	40.1	+0.1	20.1	+0.1	100.3	+0.3	%
	multi-plate	40.2	+0.2	40.3	+0.3	19.9	−0.1	100.4	+0.4	%

Discussion

The solubility conditions of the $CuSO_4$–H_2O system, illustrated as a phase diagram in Fig. 5, have been well known for a long time. It can be seen that, in the course of its decomposition $CuSO_4 \cdot 5H_2O$ melts at 95.6° (point B) and a saturated solution phase and solid $CuSO_4 \cdot 3H_2O$ are formed. This process, which actually introduces the dehydration, cannot be recognized in the conventional thermoanalytical curves (Figs 2/a–h). This can be explained as follows.

The courses of the TG curves in Figs 2/a, b, c, e and f prove that in the given cases the $CuSO_4 \cdot 5H_2O$ completely lost the first two molecules of water of crystallization before reaching 95.6°. In these cases the decomposition reaction gave gas and solid-phase products:

$$CuSO_4 \cdot 5H_2O_{(s)} \xrightarrow{95.6^\circ} CuSO_4 \cdot 3H_2O_{(s)} + 2H_2O_{(g)} \qquad (1)$$

This is attributable to the fact that, due to the slow supply of water vapour and the relatively good ventilation of the conventional crucibles, the partial pressure of the vapour within the crucible stayed low, thereby decreasing the temperature of the transformation.

In the TG curves in Figs 2/d, g and h, even three processes can be identified. Under the given circumstances, only part of the $CuSO_4 \cdot 5H_2O$ can decompose according to Eq. (1).When the temperature of the sample reached 95.6°, the $CuSO_4 \cdot 5H_2O$ which had not yet decomposed melted, and besides the solid $CuSO_4 \cdot 3H_2O$ a saturated solution appeared (Eq. (2)). However, the quantity of this was small: at most 20% of the original amount of $CuSO_4 \cdot 5H_2O$. Due to the low partial pressure of the water vapour at the moment of its appearance, this solution immediately evaporated (Eq. (3)). Accordingly, the melting (Eq. (2)) and evaporation (Eq. (3)) overlapped completely in a strictly parallel way:

$$CuSO_4 \cdot 5H_2O_{(s)} \xrightarrow{95.6^\circ} CuSO_4 \cdot 3H_2O_{(s)} + \text{sat. solution} \qquad (2)$$

$$\text{sat. solution} \xrightleftharpoons{103^\circ} CuSO_4 \cdot 3H_2O_{(s)} + 2H_2O_{(g)} \qquad (3)$$

$$CuSO_4 \cdot 3H_2O_{(s)} \xrightleftharpoons{116^\circ} CuSO_4 \cdot H_2O_{(s)} + 2\,H_2O_{(g)} \qquad (4)$$

However, the first step of the decomposition took place in a different way when the simultaneous curves were traced by using the conical crucible (Figs 2/i–m). In this case only a very small part of the $CuSO_4 \cdot 5H_2O$ decomposed before the melting of the substance, according to Eq. (1). Even this occurred only to establish the "self-generated" atmosphere, i.e. for the water vapour to carry the air away from the crucible. Since the partial processes lead to equilibrium, the partial pressure of the vapour within the crucible initially increased in parallel with the decomposition pressure of the $CuSO_4 \cdot 5H_2O$. After the melting, this increased in parallel with the tension of the saturated solution up to the boiling point. At this point, the partial pressure of the water vapour attained 100 kPa.

It should be noted that, in the given temperature domain, the air mixes with water vapour in a limited and defined ratio. Therefore, the course of the expelling of the air from inside the crucible also depends on the equilibrium of the mixing of the gases.

Accordingly, the conical crucible delayed the departure of the water vapour up to 103° (TG and DTG curves in Figs 2/i–m). Due to the special design of this crucible, the evaporation of the saturated solution took place during its boiling completely separated from the melting, as shown by the "onset" temperatures at 95° and 103° of the DTA peaks in Fig. 2/1. A comparison of the DTA curves in Figs 2/i–m further shows that the extent of separation of the two processes depended on the heating rate.

The above picture is in full accordance with the courses of the curves traced by using the quasi-isothermal heating technique. The Q–DTA' curve in Fig. 4/b shows an endothermic peak with an "onset" temperature of 95°. In contrast, in the Q–DTA' curve in Fig. 4/a this peak is missing. This is understandable, since in the former case, when the conical crucible was applied, the departure of the first two water molecules occurred at a higher temperature than the melting at 95°, according to Eqs (2) and (3), while in the latter case, when the simple covered crucible was used, this took place at a lower temperature according to Eq. (1).

A detailed study of the curves in Figs 4/b, c and d, curves 4–6 in Fig. 3 and curves A–H in Fig. 4 clearly shows that, with the application of the conical or labyrinth crucible and the quasi-isothermal heating technique, the investigations can be carried out under nearly ideal conditions (a self-generated gas atmosphere with about 100 kPa partial pressure, quasi-isothermal, quasi-isobaric and quasi-equilibrium conditions).

To return to the analysis of the DTA curve in Fig. 2/i, it turns out that under the given conditions the saturated solution began to boil at the theoretical temperature of 103°, and the boiling ended without any temperature change, despite the phenomenon (to be seen in the DTA peak) that the boiling processes appeared to end at 116°. The melting also apparently extended over a relatively wide temperature range (95–103°). This phenomenon is well known to thermoanalysts. If the temperature is raised continuously, even as slowly as in the present case, i.e. 0.2 deg min^{-1}, the system is not able to take up the transformation heat from the surrounding in time. With the quasi-isothermal heating technique, just sufficient time can be ensured for the absorption of the necessary heat amount, as proved by the courses of the curves in Figs 3 and 4. Of these curves, the most easily understandable example is to be seen in curve 4 in Fig. 3, illustrating the well known boiling process of water. According to this, under the given conditions the water began to boil at 99° and the boiling ended without any temperature change.

The condition must be explained that, despite the application of the quasi-isothermal heating technique, the peak in Fig. 4/b, indicating the melting process, showed a similar course to that of conventional DTA curves (Fig. 2/i) and extended over a relatively broad temperature interval (95–103°). This phenomenon is due to the circumstance that, up to 103°, the control system had raised the temperature in the conventional way with uniform rate, and only thereafter, when the weight change began, did the Q–DTG signal take over the role of regulation. Accordingly, the Q–DTA' curve was produced as a result of a heterogeneous regulating technique. The temperature curve would show the melting process to be an isothermal process only if the heating control were performed with the help of the DTA signal. The development of such a control technique is in progress.

It can be presumed that, with the two kinds of decomposition mechanism for $CuSO_4 \cdot 5H_2O$, it can also be explained why in the first decomposition step less water departed than stoichiometrically expected, while in the second step the excess of the departing water was just equal to the amount of water missing from the record of the first step when the conical or labyrinth crucible was applied (Tables 1 and 2). When the conventional sample holders were used, the decomposition took place in the regular way. This can be explained as follows. In the former case the intermediate $CuSO_4 \cdot 3H_2O$ was formed in the presence of a saturated solution, and therefore more water could be incorporated into the lattice structure, while in the conventional sample holders the reaction involved solid and gaseous phases under different conditions of lattice formation.

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References

1 J. Paulik, F. Paulik and M. Arnold, Thermochim. Acta, 107 (1986) 375.

2 J. Paulik, F. Paulik and M. Arnold, J. Thermal Anal., 32 (1987) 301.

3 J. Paulik and F. Paulik, Simultaneous Thermoanalytical Examinations' by Means of the Derivatograph, in Wilson–Wilson's Comprehensive Analytical Chemistry, ed. G. Svehla,, Vol. XII, ed. W. W. Wendlandt, Elsevier, Amsterdam 1981.

4 F. Paulik and J. Paulik, Thermochim. Acta, 100 (1986) 23.

5 J. Paulik and F. Paulik, Thermochim. Acta, 3 (1971) 13.

6 F. Paulik and J. Paulik, J. Thermal Anal., 5 (1973) 253.

Zusammenfassung — Der Mechanismus der thermischen Zersetzung von $CuSO_4 \cdot 5H_2O$ wird durch experimentelle Bedingungen in grossem Masse beeinflusst. Unter herkömmlichen Bedingungen, in einem offenen Tiegel, spielt sich die erste Teilreaktion in einem Schritt ab und hat sowohl feste als auch gasförmige Produktephasen zur Folge. Wird ein Probenhalter benutzt, der eine selbstgenerierte Atmosphäre erzeugt, wird die Reaktion in zwei konsekutive Vorgänge unterteilt. Zuerst schmilzt die Probe inkongruent, die dabei entstandene gesättigte Lösung (neben festem $CuSO_4 \cdot 3H_2O$) dampft dann beim Verkochen ein. Diese beiden Vorgänge können mittels der DTA-Kurve vollkommen voneinander unterschieden werden. Die Selektivität der Untersuchung kann durch Anwendung der quasi-isothermen Heiztechnik weiter verbessert werden.

Die zwei Zersetzungsarten stimmen mit der Beobachtung überein, dass bei der Zersetzung nach dem ersteren Mechanismus das Zwischenprodukt $CuSO_4 \cdot 3H_2O$ eine stöchiometrische Zusammensetzung besitzt, während es im letzteren Fall stets ungefähr 2,5% Wasser mehr enthält, als berechnet.

Резюме — Механизм термического разложения пентагидрата сульфата двухвалентной меди в значительной мере затрагивается экспериментальными условиями. При обычных условиях в открытом тигле имеет место первая частичная реакция, протекающая в одну стадию с образованием твердой и газообразной фаз. При использовании держателя образца с самогенерируемой атмосферой, реакция разделяется на два последовательных процесса. Сначала образец инконгруэнтно плавится, а затем образующийся насыщенный раствор, кроме твердого тригидрата сульфата меди, испаряется при кипении. Эти два процезза могут быть полностью различимы на кривой ДТА. Селективность такого разделения может быть увеличена путем применения метода квазиизотермического нагрева. Эти два типа разложения коррелируются с тем явлением, что если разложение протекает по первому механизму, то образующийся промежуточный тригидрат сульфата меди имеет стехиометрический состав. Если же разложение протекает по второму механизму, то образующееся соединение содержит количество воды на 2,5% больше вычисленного.