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STATISTICAL ANALYSIS OF ENTHALPY DETERMINATION RESULTS RELATING TO THE DEHYDRATION PROCESS OF $CuSO_4 \cdot 5H_2O$

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Methods of variance analysis were utilized to select the conditions used in DSC studies of dehydration processes of various copper sulphate hydrates. The constant methodical errors were determined. Procedures were pointed out to increase the accuracy of DSC measurements in dehydration processes.

A vast number of papers have dealt with both the mechanism and the thermochemical characteristics of dehydration reactions, owing to their frequent occurrence [1, 2].

The most widespread methods for studying such reactions are thermoanalytical; for quantitative determinations of the thermochemical values in dehydration processes, differential scanning microcalorimetry (DSC) appears most suitable of all [1].

However, the complexity of dehydration processes and the diversity of factors acting on their course necessitates a careful selection of the experimental conditions and careful analysis of the results. Among the most important factors acting both on the shape of the thermoanalytical curves and on the experimentally obtained thermochemical values, the following should be pointed out.

First, it should be remembered that dehydration processes proceed in stages and that the number of intermediate phases may be rather high. The operations for separating the individual hydrated phases and the determination of their thermodynamic functions make it compulsory to take into account kinetic factors, by reason of the pseudo equilibria readily established in the hydrates [2].

Secondly, dehydration processes result partly in the formation of X-ray-amorphous products, and the excess energy of the non-regular arrangement in the amorphous phase varies within 3 to 7 kcal/mol [3, 4]; this may introduce significant errors into the calculations of dehydration heats.

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Thirdly, the experimental conditions, and above all the pressure and composition of the gas phase, have a great effect on the chemistry of the dehydration and consequently on the energy relationships of the process.

It is known [2] that a high water vapour pressure favours the crystallization of amorphous products and, in contrast, dehydration carried out in vacuum leads to the formation of amorphous products.

Two parallel reactions of copper sulphate pentahydrate dehydration may proceed in water vapour [5]:

$$\begin{tikzcd}
 & CuSO_4\cdot 3H_2O+2\ H_2O \\
CuSO_4\cdot 5H_2O \arrow[ur] \arrow[dr] & \\
 & CuSO_4\cdot H_2O+4\ H_2O
\end{tikzcd}$$

All these particular features of dehydration reactions cause difficulties in the obtaining of satisfactorily accurate and reproducible thermochemical values by DSC.

The purpose of this paper is to find objective criteria for selecting the experimental conditions in dehydration heat determinations by DSC.

We have studied the dehydration processes of certain copper sulphate hydrates. Various reasons favoured the choice of these substances for the study.

First of all, the thermal dehydration reactions

$$1/2\ CuSO_4\cdot 5H_2O \rightarrow 1/2\ CuSO_4\cdot 3H_2O+H_2O+\Delta H_1 \tag{I}$$

$$1/2\ CuSO_4\cdot 3H_2O \rightarrow 1/2\ CuSO_4\cdot H_2O+H_2O+\Delta H_2 \tag{II}$$

$$CuSO_4\cdot H_2O \rightarrow CuSO_4+H_2O+\Delta H_3 \tag{III}$$

have been studied in great detail [1, 2, 5, 6]; the thermodynamic characteristics [7] and the structures of both the initial compounds and the products of these reactions are well known.

Secondly, the intermediate hydrates can be synthetized in a simple manner [6] and identified unequivocally by X-ray analysis.

Thirdly, the dehydration process of $CuSO_4\cdot 5H_2O$ presents all the particular features of dehydration: a multistage process, a possible mechanism change under changed experimental conditions [5], the possible formation of X-ray-amorphous products, and the non-stoichiometric compositions of both the initial substance and the intermediates.

Experimental

Various copper sulphate hydrates were used in the experiments.

Analytical grade copper sulphate pentahydrate was used in the form of crystals of ~1 mm^3, and in the form of powder consisting of particles 0.20–0.25 mm in diameter. Specimens after long storage and also freshly recrystallized specimens were used.

Two intermediate hydrates, $CuSO_4 \cdot 3H_2O$ and $CuSO_4 \cdot H_2O$, were prepared by methods described in the literature [6]. The compositions of the compounds obtained were controlled by X-ray analysis. For this purpose a DRON-2 diffractometer was applied, using cobalt K_α radiation, and the results obtained were compared with ASTM data.

The hydrate composition of the samples is of great importance in the determination of dehydration heats. For the determination of hydrate composition, thermogravimetry was applied, using an OD-103 derivatograph. The sample mass was 100 mg, and the heating rate was 5 deg/min. Platinum crucibles were used as sample holders. The experiments were carried out in static air atmosphere. From the thermogravimetric data, the compositions of the compounds employed for the study were as follows:

a $CuSO_4 \cdot 4.88H_2O$ — powdered sample
a' $CuSO_4 \cdot 5.00H_2O$ — powdered sample, freshly recrystallized
b $CuSO_4 \cdot 5.07H_2O$ — single-crystals
c $CuSO_4 \cdot 3.02H_2O$ — powdered sample
c' $CuSO_4 \cdot 2.98H_2O$ — powdered sample, freshly prepared
d $CuSO_4 \cdot 1.01H_2O$ — powdered sample, freshly prepared

An accurate knowledge of the hydrate number is necessary for the determination of dehydration heats, since the very high heat of evaporation of water would cause great errors in the calculated dehydration heats in the event of incorrect hydrate numbers.

A DSM-2 differential scanning microcalorimeter was applied for dehydration heat determinations. The sample holders were standard aluminium dishes fitted with perforated lids.

The DSC experiments were carried out under the following conditions:

e — static air atmosphere, initial temperature 20°, $p_{H_2O} = 9$ Torr in the environment, sample mass 6 to 8 mg, heating rate 6 deg/min;
f — air flow saturated with water vapour, $p_{H_2O} = 17$ Torr, sample mass 6 to 8 mg, heating rate 6 deg/min;
g — residual pressure 30 Torr;
h — sample mass 6 to 8 mg, heating rate 3 deg/min;

i — sample mass 6 to 8 mg, heating rate 12 deg/min;
k — sample mass 30 mg, heating rate 6 deg/min.

In all experiments with $CuSO_4 \cdot 5H_2O$ samples, the calorimetric block was cooled to 20° after each determination. The control of the initial temperature of the calorimetric block is necessary to avoid spontaneous dehydration, since the dissociation pressure of $CuSO_4 \cdot 5H_2O$ may be higher at the given temperature than the water vapour pressure in the environment.

Under the above conditions, we determined the dehydration heats of reaction I, reaction II, reactions I + I and reaction III. The results obtained were recalculated for 1 mol water evolved.

Table 1 presents the mean values of n determinations of ΔH, kcal/mol H_2O, for reactions I, II and III, the mean values for the overall enthalpies of reactions I + II, and the standard deviations σ_i of these means. The reason for giving the overall enthalpies of reactions I + II is that under certain conditions the dehydration effects of I and II in the DSC curver overlap.

Results and discussion

The results presented in Table 1 differ essentially in some cases. One may assume that such differences are due not to reproducibility error changes, but to the effect of the experimental conditions on the dehydration heat values.

To carry out variance analysis, it is a necessary condition that the variance should be homogeneous for all series of measurements. To check the homogeneity of variance, for each reaction we calculated the value F, the ratio of the maximum and minimum variances:

$$F_{\mathrm{exp}} = \frac{\sigma^2_{\mathrm{max}}}{\sigma^2_{\mathrm{min}}}$$

In those cases where $F_{\mathrm{exp}} > F_{\mathrm{theor}}$ for a 5% significance level, the corresponding values of ΔH and σ_{max} were discarded and subsequently left out of consideration. These values are denoted by * in Table 1.

The remaining ΔH values for each reaction may be regarded as random values of one general mean. If this is the case, then (by analyzing the distribution r of the relative deviations by means of the criteria r_{min} and r_{max}) some sharply deviating results will be found which may also be left out of consideration. For this purpose we calculated the values

$$r_{\mathrm{max}} = \frac{\Delta \bar{H}_i^{\mathrm{max}} - \Delta \bar{H}}{\sigma_{\Delta \bar{H}} \sqrt{\frac{n-1}{n}}}$$

Table 1 Copper sulphate dehydration reactions: mean values of enthalpies $\Delta \bar{H}_i$, kJ/mol H_2O

Compound	Conditions		Reaction											
			I			II			I+II			III		
			$\Delta \bar{H}_i$	σ	n	$\Delta \bar{H}_i$	σ	n	$\Delta \bar{H}_i$	σ	n	$\Delta \bar{H}_i$	σ	n
$CuSO_4 \cdot 5H_2O$	*a*	*e*	58.31	0.9	9	45.14*	1.0	9	54.1*	0.9	8	43.05*	1.4	9
		f	54.34	1.0	6	50.16	0.4	6	52.25	0.5	6	56.85*	3	6
		g							51.4	0.4	9			
		h	53.08	0.7	5	50.16*	0.9	5	51.4	0.8	5	60.2*	0.9	5
		i							53.5	0.8	5	57.3	0.8	5
$CuSO_4 \cdot 3H_2O$	*b*	*e*							56.4	0.5	5			
		g							55.2	0.6	8			
	b′	*e*							55.2	0.3	5			
	a	*e*	57.26	0.7	4	48.49**	0.8	4	52.7	0.6	5	56.43*	1	5
$CuSO_4 \cdot H_2O$	*c*	*e*				53.92**	0.8	5				54.34**	0.5	5
		f				52.25**	0.3	4				55.2	0.3	4
		g				57.68	0.2	5				44.7**	0.7	5
		h				52.25	0.9	5				57.7	0.8	5
		i				48.9	0.4	3				56.0	1.0	3
		k				50.58	0.2	5				63.2	0.6	4
	c′	*g*				57.05	0.2	4				41.2*	0.5	4
		e				55.2	0.5	5						
	d	*e*										60.4**	0.3	9
		f										67.7	0.18	5
		g										67.3	0.18	5
		h										64.4	0.5	5
		i										69.0	0.1	5
		k										68.5	0.04	

and

$$r_{min} = \frac{\Delta \bar{H} - \Delta \bar{H}_i^{\min}}{\sigma_{\Delta \bar{H}} \sqrt{\dfrac{n-1}{n}}}$$

where $\Delta \bar{H}_i$ are the enthalpy values listed in Table 1 for each reaction; $\Delta \bar{H}$ is the mean of all $\Delta \bar{H}_i$ values for each individual reaction; $\Delta \bar{H}_i^{\max}$ and $\Delta \bar{H}_i^{\min}$ are the extreme values of $\Delta \bar{H}_i$ for each individual reaction; $\sigma_{\Delta \bar{H}}$ is the standard deviation of $\Delta \bar{H}$, determined as the weighted mean of the standard deviations of $\Delta \bar{H}_i$; and n is the mean number of $\Delta \bar{H}$ measurements.

In those cases when the calculated values of $r_{\max}$ or r_{min} were higher than the corresponding theoretical value for the 1% significance level, the measured data were discarded. These values are denoted by ** in Table 1.

This preliminary statistical processing of the experimental results allowed the exclusion even in the first stage of a number of results inadequate relative to the other results.

The variance analysis proper was performed using the relative values

$$y=\frac{\Delta H_i-\Delta H_{\mathrm{theor}}}{\Delta H_{\mathrm{theor}}} \tag{2}$$

where $\Delta H_{\mathrm{theor}}$ are the dehydration heats of the reactions studied, computed from the formation heats of the initial substances and the reaction products [7]. The values $\Delta H_{\mathrm{theor}}$ were reduced to the temperature of the experiment; they are listed in Table 2.

The study of the new variable allows determination of the value of the constant methodical error.

Table 2 Results of variance analysis for selecting experimental conditions for enthalpy determinations by DSC in $CuSO_4 \cdot nH_2O$ dehydration processes ($n=5$; 3; 1), methodical error β and standard deviations of reproducibility and random methodical error

Reaction	Conditions	ΔH, kJ/mol	β, rel. %	$\sigma_{\mathrm{repr.gen}}$, rel. %	$\sigma^*_{\mathrm{rand\,meth}}$, rel. %	$\Delta H_{\mathrm{theor}}$, kJ/mol [7]
I	*ae* *af* *ah* *d'e*	55.8	0.3	6.0	3.0	57.47
II	*cg* *c'g* *c'e*	56.64	1.0	2.5	2.0	56.01
I+II	*ai* *be* *bg* *a'e* *b'e*	54.76	3.0	4.5	1.75	56.85
III	*df* *dg* *dk*	68.13	3.0**	3.5	1.20	69.8

* All values of $\sigma_{\mathrm{rand\,meth.gen}}$ are insignificant compared to $\sigma_{\mathrm{repr.gen}}$

** See in the text

The strategy of selecting optimum experimental conditions is as follows: first, we divide the overall variance into two values:

$$\sigma_\Sigma^2 = \frac{\sigma_{repr}^2}{n} + \sigma_{\text{rand meth}}^2 \tag{3}$$

where σ_{repr} is the standard deviation of reproductibility, defined by the experimental technique, and $\sigma_{\text{rand meth}}$ is the deviation due to the inhomogeneity of the values, defined by the differing conditions, and termed by us "random methodical deviation".

It may be stated that homogeneous results will be obtained when $\sigma_{\text{rand meth}}^2$ is insignificant compared to σ_{repr}^2. By carrying out variance analysis and discarding those results in which $\sigma_{\text{rand meth}}^2$ is significant, we obtained values independent of the method by which they were obtained, that is, independent of the experimental conditions.

For determination of the significance of $\sigma_{\text{rand meth}}^2$, the following relationship was used:

$$F'_{\text{exp}} = \frac{\dfrac{\sigma_{\text{repr}}^2}{n} + \sigma_{\text{rand meth}}^2}{\dfrac{\sigma_{\text{repr}}^2}{n}} \tag{4}$$

at $(m-1)$ degrees of freedom for the numerator and $m(n-1)$ degrees of freedom for the denominator, where m is the number of methods applied for the experimental determination and n is the mean number of $\Delta\bar{H}_i$ determinations.

For each process studied a variance table was set up, in which the values y obtained under the different experimental conditions were arranged in columns. This arrangement of the data yields the value of the constant methodical error as the overall mean of the total table; the variance between the columns is defined by the relative methodical errors due to the specific experimental conditions; the variance between the lines is defined by the relative errors of reproducibility [8]. The values σ_{repr} and $\sigma_{\text{rand meth}}$ are determined by the small number of measurements. The upper possible limit for these errors in the general set, from which this random small selection was taken, is expressed by the following equations:

$$\sigma_{\text{gen.repr}} = \frac{\sqrt{m(n-1)}}{\sqrt{\chi^2}} \cdot \bar{\sigma}_{\text{repr}} \tag{5}$$

$$\sigma_{\text{gen.rand meth}} = \frac{\sqrt{m}}{\sqrt{\chi^2}} \bar{\sigma}_{\text{rand meth}}$$

where χ^2 is the value of the χ^2 criterion for the corresponding degrees of freedom and the confidence interval $\alpha = 95\%$.

The constant methodical error β is significant if the following inequality holds:

$$\beta \geqslant \frac{t\sqrt{\dfrac{\sigma^2_{\mathrm{repr}}}{n} + \sigma^2_{\mathrm{rand\,meth}}}}{\sqrt{m}} \tag{6}$$

where t is the Student criterion.

The variance analysis carried out using both they y values and the ΔH_i values gave the results listed in Table 2. They demonstrate that the method described in this paper allows an objective selection not only of the dehydration enthalpy values, but also of the optimum experimental conditions. These conditions may also be optimal for studying the dehydration processes of compounds similar to copper sulphate pentahydrate.

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Zusammenfassung — Methoden der Varianzanalyse werden angewandt, um die Auswahl der Bedingungen zur Untersuchung des Dehydratisierungsprozesses verschiedener Kupfersulfat-Hydrate mittels DSC zu treffen. Die konstanten methodischen Fehler wurden ermittelt. Es wird auf Verfahren zur Erhöhung der Genauigkeit von DSC-Messungen bei Dehydratisierungsprozessen hingewiesen.

Резюме — С помощью методов дисперсионного анализа проведен выбор условий ДСК-эксперимента по определению энтальпий процессов дегидратации различных гидратов сульфата меди. Определены постоянные методические ошибки. Намечены пути повышения точности ДСК-эксперимента при определении энтальпий процессов дегидратации.