On the nature of crystallization water using thermal analysis. - The application to some hydrates with different cations

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The nature of the crystallization water in some hydrates with different cations, namely: $MnSO_4 \cdot H_2O$; $FeSO_4 \cdot 7H_2O$; $CoSO_4 \cdot 7H_2O$; $NiSO_4 \cdot 7H_2O$, has been studied by the application of the following non-isothermal techniques: thermogravimetry (TG), derivative thermogravimetry (DTG), and differential thermal analysis (DTA). Analysis of the characteristic thermogravimetric data (T_m, W) and of the kinetic parameters (n, E_a) calculated from DTG and DTA data - with $CuSO_4 \cdot 5H_2O$ as a reference - demonstrated the existence of crystallization and anion water in the studied hydrates. The activation energy of the process of anion water elimination does not depend on the nature of the cation. This conclusion was confirmed by the absence of the compensation effect in this process.

Keywords: crystallization water, TG–DTG–DTA, kinetics, hydrates.

Our previous papers[1,2] dealt with the influence of the anion – with a common cation - on the process of anion water elimination. In the present study, the influence of the nature of the cation, with a common anion (*i.e.*, SO_4^{2-}),[3] was investigated. In $MSO_4 \cdot 7H_2O$ hydrates, where M denotes Fe, Co or Ni, (heptahydrates) and $MnSO_4 \cdot H_2O$ (monohydrate), the crystalline structures of the investigated hydrates are isomorphous.[4]

The values of the kinetic parameters of the process of anion water elimination, calculated from DTG[5,6] and DTA[7–9] data, do not depend on the operational conditions, such as heating rate, air or N_2 atmosphere. The study of compensation parameters[10–12] for this stage showed that the activaiton energy does not vary with $\ln A_m$ which was also confirmed by the Arrhenius plots $k = f(1/T)$. These facts lead to the conclusion that the anion water hydrogen bond is the same in all the studied hydrates, independent of the nature of the cation.

EXPERIMENTAL

I. — Paulik-Paulik-Erdey/MOM Budapest derivatograph, enabling the simultaneous recording of T, TG, DTG and DTA curves. Recording conditions: sample mass » 100 mg, heating rate = 12 °C/min,

maximum temperature = 1000 °C, DTG and DTA sensitivity 1/10, reference material Al₂O₃, freshly calcinated at 1000 °C in an air atmosphere.

II. — Mettler TA-1 No. 80 thermobalance, enabling the simultaneous recording of T, TG, DTG and DTA curves under a dynamic N_2 atmosphere of 30 ml/min. Recording conditions: sample mass » 10 mg, heating rate = 10 °C/min, maximum temperature 600 °C, DTG and DTA sensitivity 1/10, reference material Al₂O₃, freshly calcinated at 1000 °C.

III. — Thermogravimetric TGA - 2910 Du Pont, Canada balance, enabling the simultaneous recording of TG and DTG curves. Recording conditions: sample mass = 55.017 mg, heating rate = 10 °C/min, maximum temperature = 600 °C, dynamic nitrogen atmosphere at 30 ml/min.

The hydrates studied, $CuSO_4 \cdot 5H_2O$ ($M = 249.68$ g/mol), $MnSO_4 \cdot H_2O$ * ($M = 169.01$ g/mol), $FeSO_4 \cdot 7H_2O$ ($M = 278.02$ g/mol), $CoSO_4 \cdot 7H_2O$ ($M = 281.1$ g/mol) and $NiSO_4 \cdot 7H_2O$ ($M = 280.06$ g/mol), were supplied by Merck and Prolabo (*).

The size of the hydrate granulates analyzed was in all cases 40 mesh.

RESULTS AND DISCUSSION

The TG and DTG curves recorded with device I are shown in Figs. 1 and 2. These Figs. and Table I show that the elimination of water occurs in two well-distinct stages, regardless of the atmosphere and the sample mass. This observation is in agreement with literature data in which it was reported that other heptahydrates,
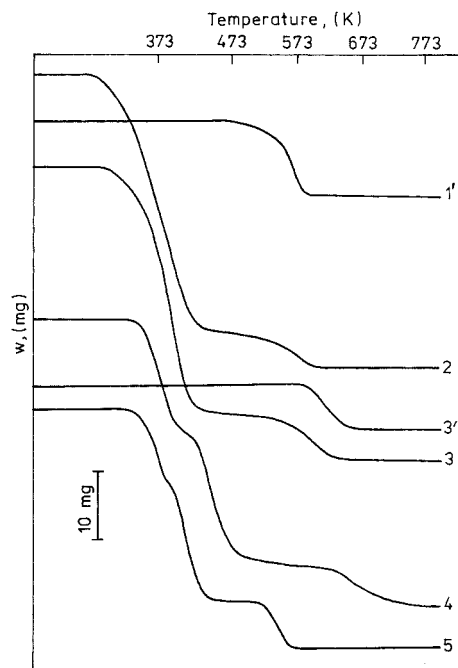

Fig. 1. TGA curves of hydrates 1 – 4 recorded on installation I.
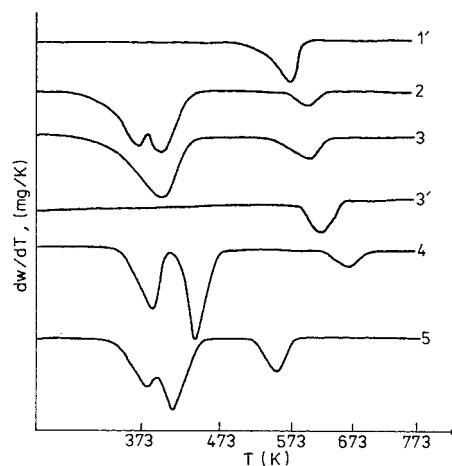
Fig. 2. DTG curves of hydrates 1 – 4 recorded on installation I.

$ZnSO_4 \cdot 7H_2O$[13,16] and $MgSO_4 \cdot 7H_2O$[14,15], behave in a similar manner, even at the low heating rates of 3 °C/min[13] and 5 °C/min.[14–16]

The characteristic temperatures and mass losses from DTG and TG measurements obtained on instruments I and II are presented in Table I. Comparing these data with data for $[Cu(H_2O)_4]^{2+}(SO_4 \cdot H_2O)^{2-}$ (Fig. 3), it would seem that 6 molecules of crystallization water are eliminated in the first stage (samples 2, 3 and 4) and a molecule of anion water remains that is eliminated in the final step, as the temperature ranges are the same for all samples.

TABLE I. Characteristic thermogravimetric values

| No. | Sample | A_p | Sample mass (mg) | Step I | | | Step II | | | | W_t mg | W_{exp} mg |
				$T_i/°C$	$T_f/°C$	No.Mol. H_2O	$T_i/°C$	$T_m/°C$	$T_f/°C$	No.Mol. H_2O		
1'	$MnSO_4 \cdot H_2O$	I(air)	103.4	–	–	–	232	295	320	1	11.01	11.11
2	$FeSO_4 \cdot 7H_2O$	I(air)	95.9	29	153	6	291	320	348	1	6.21	5.26
		II(N$_2$)	10	45	464	6	253	278	317	1	0.65	0.67
3	$CoSO_4 \cdot 7H_2O$	I(air)	95.9	75	204	6	289	343	362	1	6.14	6.43
		II(N$_2$)	10	32	180	6	210	295	340	1	0.64	0.68
3'	$CoSO_4 \cdot H_2O$	I(air)	92.5	–	–	–	316	348	387	1	9.62	8.77
4	$NiSO_4 \cdot 7H_2O$	I(air)	98.6	65	226	6	340	383	455	1	6.32	6.43
		II(N$_2$)	10	88	224	6	369	396	429	1	0.64	0.6
5	$CuSO_4 \cdot 5H_2O$	I(air)	102.4	48	165	4	244	281	305	1	7.37	7.6
		II(N$_2$)	10	57	165	4	238	265	295	1	0.72	0.75
		III(N$_2$)	55.017	68	183	4	205	250	285	1	3.96	4.03

T_i = initial temperature; T_m = temperature corresponding to the maximum rate of mass loss; T_f= final temperature; W_t = theoretical loss; W_{exp} = experimental mass loss; A_p = type of device.

The same conclusion may be drawn from the shape of the DTG curves obtained using equipment I (Fig. 4) and also from the characteristic temperatures listed in Table II.
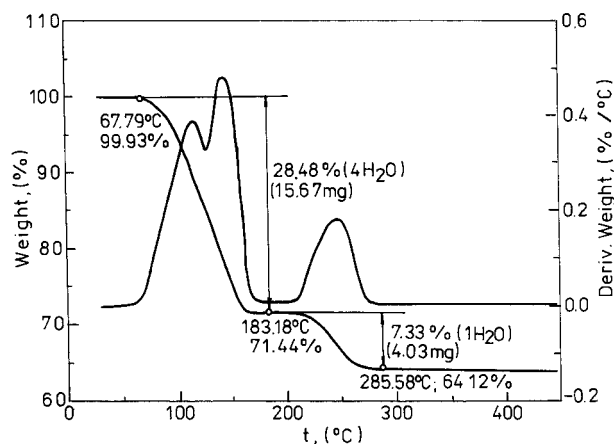

Fig. 3. TGA curve of $CuSO_4 \cdot 5H_2O$, recorded on installation III.

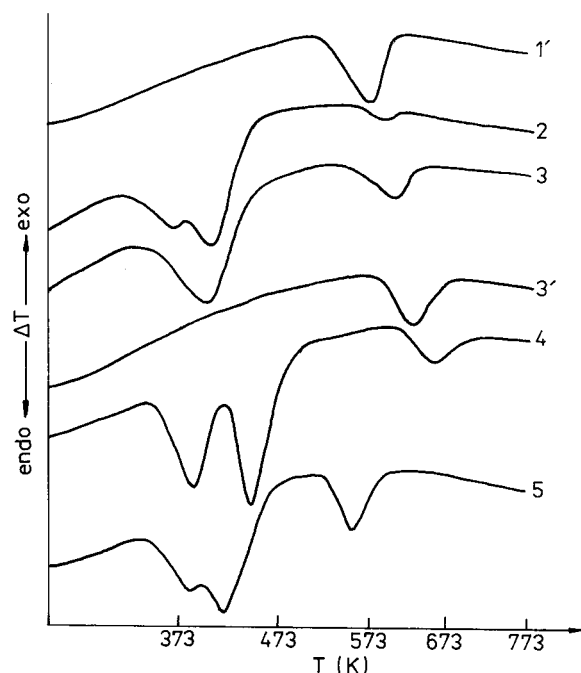Fig. 4. DTA curves of hydrates 1 – 4 recorded on installation I.

TABLE II. Characteristic vlue for DTA

No.	Sample	A_p	Step I			Step II			
			$T_i/°C$	$T_f/°C$	No.Molec. H₂O	$T_i/°C$	$T_m/°C$	$T_f/°C$	No.Molec. H₂O
1'	$MnSO_4·H_2O$	I(air)	–	–	–	232	300	337	1
2	$FeSO_4·7H_2O$	I(air)	52	177	6	291	323	353	1
		II(N₂)	60	164	6	253	278	317	1
3	$CoSO_4·7H_2O$	I(air)	75	205	6	291	355	390	1
		II(N₂)	32	182	6	260	295	340	1
3'	$CoSO_4·H_2O$	I(air)	–	–	–	315	350	416	1
4	$NiSO_4·7H_2O$	I(air)	65	226	6	350	390	448	1
		II(N₂)	88	224	6	342	396	433	1
5	$CuSO_4·5H_2O$	I(air)	79	196	4	252	284	324	1
		II(N₂)	57	165	4	228	240	282	1
		DSC(air)	57	162	4	211	243	286	1

T_i = initial temperature of the DTA peak; T_m = temperature at the maximum of the DTA peak; T_f = final temperature of the DTA peak; A_p = type of device.

It can be seen from Tables I and II that the temperature domain over which the water molecule from $MnSO_4·H_2O$ and $CoSO_4·H_2O$ monohydrates corresponds to the elimination of anion water.

Due to the complexity of the process of the elimination of crystallization water, and to the fact that our main interest lay in the anion water, only the activation

energy for the last step, the elimination of anion water, was evaluated by differential and integral methods using DTG and DTA data for the same interval of the extent of the reacton ($a = 0.2 - 0.8$).

The determined activation energies for this step are listed in Table III, from which it can be seen that the activation energies for all the studied samples may be considered constant. From this fact it follows that the activation energy associated with the eliminiation of the last water molecule is independent of the nature of the cation. For the hydrates under investigation this justifies its name – anion water.

TABLE III. Kinetic parameters for the last step of dehydration ($a = 0.2$–0.8)

No.	Sample	\multicolumn{6}{c}{DTG}	\multicolumn{12}{c}{DTA}
		\multicolumn{3}{c}{FC}	\multicolumn{3}{c}{CR}	\multicolumn{3}{c}{FC}	\multicolumn{3}{c}{CR}	\multicolumn{3}{c}{F}	\multicolumn{3}{c}{k_i}
		n	E_a (kJ/mol)	R	n	E_a (kJ/mol)	R	n	E_a (kJ/mol)	R	n	E_a (kJ/mol)	R	n	E_a (kJ/mol)	R	n	E_a (kJ/mol)	R
1′	MnSO$_4$·H$_2$O	0.8	164	0.98	1	140	0.99	1	182	1	1	189	1	1	176	1	1	195	0.99
2	FeSO$_4$·7H$_2$O	0.8	209	0.97	1	193	0.99	1	172	0.83	1	196	1	1	184	0.97	1	215	0.89
3	CoSO$_4$·7H$_2$O	0.9	187	0.96	1	169	0.99	1	163	0.99	1	177	1	1	173	1	1	208	1
4	NiSO$_4$·7H$_2$O	0.9	206	0.92	1	166	0.98	1	178	0.98	1	195	0.99	1	180	0.98	1	182	0.94
5	CuSO$_4$·5H$_2$O	1.1	196	0.97	1	216	1	1	191	0.99	1	199	0.99	1	189	0.94	1	197	0.87

FC = the Freeman-Carroll method; CR = the Coats Redfern method; F = the Fatu method; k_i = the method of kinetic parameter determination from the initial rate constants; R = the correlation coefficient for the linear regression; n = the reaction order; E_a = activation energy.

In order to check this conclusion, the compensation parameters introduced by Nicolaev[10] and Gorbachev[11] were calculated (see Table IV). The compensation parameters a, b and S_p can be considered constant[17,18] which indicates that the bond is of the same type. From Fig. 5, which shows a plot of $\ln A$ *versus* E_a, it can be seen that the points converge to a restricted area indicating the lack of a kinetic compensation effect (KCE). This is the case when the breaking link is the same – *i.e.*, the molecule of water is bound through hydrogen bridges of the same strength.

TABLE IV. The compensation parameters

No. crt.	Hydrate	$DT=T_f-T_i$	T_m (K)	E_a (kJ/mol)	$S_p = E_a/\ln A$ (kJ/mol)	\multicolumn{3}{c}{Nikolaev}	\multicolumn{2}{c}{Gorbachev}
						$a \cdot 10.000$ (mol/J)	b	$\ln A$	T_{cr}(k)	ln/A
1'	MnSO$_4$·H$_2$O	88	568	188	4.747	2.12	−0.195	39.7	571	39.7
2	FeSO$_4$·7H$_2$O	62	582	199	4.858	2.07	−0.188	40.9	584	40.9
3	CoSO$_4$·7H$_2$O	73	616	194	5.164	1.95	−0.327	37.5	621	37.5
4	NiSO$_4$·7H$_2$O	115	660	200	5.557	1.82	−0.437	35.9	668	35.9
5	CuSO$_4$·5H$_2$O	70	554	189	4.62	2.17	−0.137	41	556	41

T_m = Temperature at maximum rate; E_a = the mean activation energy; T_{cr} = isokinetic temperature; A = the pre-exponential factor.
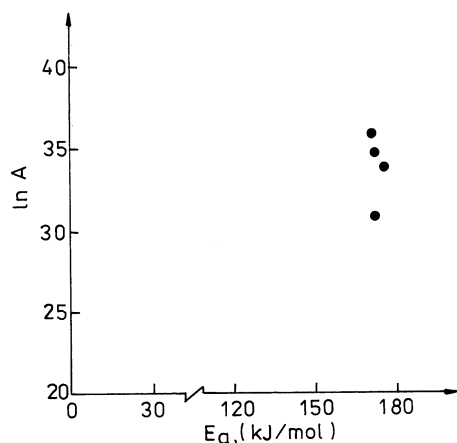
Fig. 5. The ln A = f (E_a) dependence for the last stage of dehydration of hydrates 1 – 4.

A clear confirmation of such a conclusion can be gained from the Arrhenius plots,[19] Fig. 6, in which the parameter k is plotted as a fuction of 1/T. A series of parallel straight lines, with correlation coefficients ranging between 0.97788 and 0.9955, results. From the Arrhenius plots, constant values of the activation energy of the second step of dehydration are obtained that agree with the values listed in Table II.
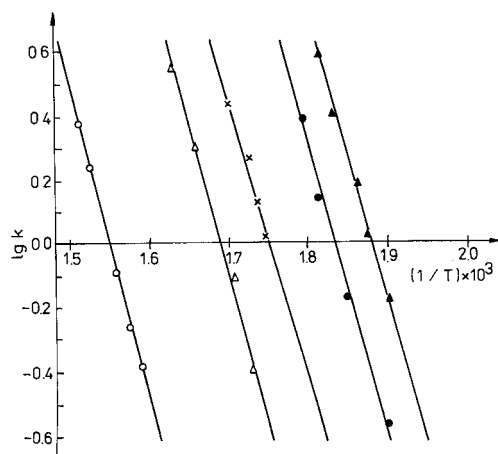

Fig. 6. The ln k = 1/T dependence for the last dehydration stage: (■) $MnSO_4 \cdot H_2O$; (▲)$FeSO_4 \cdot 7H_2O$; (✘) $CoSO_4 \cdot 7H_2O$; (●)$NiSO_4 \cdot 7H_2O$; (◆)$CuSO_4 \cdot 5H_2O$

CONCLUSIONS

The applied methods of analysis, combined with the study of the compensation effect, allow the following conclusions to be reached:

— The hydrates $FeSO_4 \cdot 7H_2O$, $CoSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 7H_2O$ contain 6 molecules of crystallization water and one molecule of anion water;

— The hydrates $MnSO_4 \cdot H_2O$ and $CoSO_4 \cdot H_2O$ contain only one molecule of anion water;

— The strength of the hydrogen bond linking the anion water depends only

negligibly on that of the coordinative bond and is not influenced by the nature of the cation;

— The study of the compensation effect supports the conclusions drawn from the values of the activation energies;

— The results obtained by the applied thermal methods supports the following generalized structure for the studied hydrates, which agree with the existing literature:[20]

$$[M(H_2O)_6]^{2+}(SO_4 \cdot H_2O)^{2-}, \text{ where } M = Fe, Co, Ni \text{ and } [Mn]^{2+}(SO^4 \cdot H_2O)^{2-}$$
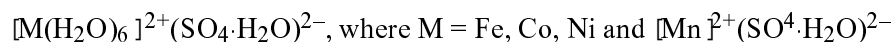
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КОРИШЋЕЊЕ ТЕРМИЈСКЕ АНАЛИЗЕ У ОДРЕЂИВАЊУ ПРИРОДЕ КРИСТАЛИ-
ЗАЦИОНЕ ВОДЕ - ПРИМЕНА НА НЕКЕ ХИДРАТЕ СА РАЗЛИЧИТИМ КАТЈОНИМА

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Природа кристализационе воде код неких хидрата са различитим катјонима, као што су $MnSO_4 \cdot H_2O$, $FeSO_4 \cdot 7H_2O$, $CoSO_4 \cdot 7H_2O$ и $NiSO_4 \cdot 7H_2O$, проучавана је применом следећих неизотермских техника: термогравиметријом (TG), деривативном термогравиметријом (DTG) и диференцијалном термијском анализом (DTA). Анализом карактеристичних термогравиметријских података (T_m, W) и кинетичких параметара (n, E_a) израчунатих из DTG и DTA података користећи $CuSO_4 \cdot 5H_2O$ као референцу, доказано је постојање кристализационе и анјонске воде у проучаваним хидратима. Енергија активације за процес уклањања анјонске воде не зависи од природе катјона. Овај закључак потврђен је одсуством компензационог ефекта код овог процеса.

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