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Eyring parameters of dehydration processes

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Abstract

Thermogravimetry was used in the study of the kinetics of dehydration of $MnSO_4{\cdot}5H_2O$, $CuSO_4{\cdot}5H_2O$ and $3CdSO_4{\cdot}8H_2O$ under static air atmosphere. The values of the kinetic and thermodynamic parameters for each stage of thermal dehydration were calculated from $\alpha(T)$ data by using the integral method, applying the Coats–Redfern approximation. The best model for all stages of dehydration is random nucleation model F1. The dependencies of enthalpy on entropy of activated complexes for different kinetic models were described. The linear relation was calculated between the Gibbs energy of activated complexes and the maximum dehydration rate temperature for analysed dehydration processes.

Keywords: Kinetics of thermal dehydration; Thermodynamic functions of activated complexes; Decomposition of hydrates of cadmium; Copper and manganese sulphates

1. Introduction

Hydrates have been known from the earliest days of chemistry, well-known minerals have interesting physical properties and have always played an important role in various technologies. A characteristic of all hydrates is that the lattice collapses when water is removed from the crystals and the structure of the anhydrous material bearing no simple relation to that of the hydrate. There are certain crystals which have the ability to absorb water which may be subsequently removed without radically altering the crystal. If the crystal consist of a rigid framework in which there are cavities or tunnels, then reversible hydration and dehydration may take place [1]. The water product is inherently volatile, but a proportion is adsorbed on the hydrophilic surface and may participate in the restructuring of the solid material, while such surface bonded water molecules may be mobile in an adsorbed state [2]. In the salt hydrates water molecules may be associated with the metal atoms or with anions and other water molecules, the metal ions may be surrounded by several different water molecules (they do not have the same environment, e.g. $NiSO_4{\cdot}7H_2O$) while two kinds of metal ions with different environments may exist in hydrates ($8CdSO_4{\cdot}3H_2O$). Hydroxyl bonds are formed in hydrated oxy-salts. The geometry of hydrate structures may determine their behaviour.

Dehydrations of crystalline solids together represent an important group of heterogeneous reactions. In one set of reactions, water, which is present as a ligand coordinated to (usually) a transition-metal cation, is released on heating. Other dehydrations are accompanied by the structural reorganization of the lattice, which is destabilized by the removal of constituent hydrogen-bonded water. There may also be hydroxyl groups that combine to give oxide and water [3]. The step-by-step character of thermal dehydration

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Nomenclature

A	pre-exponential Arrhenius factor (min^{-1})
E	apparent activation energy ($\mathrm{kJ\,mol}^{-1}$)
$f(\alpha)$	conversion function dependent on mechanism of the reaction
F	Snedecor's variable
$g(\alpha)$	integral form of the conversion function
ΔG^*	Gibbs free energy of activated complexes ($\mathrm{kJ\,mol}^{-1}$)
ΔH^*	enthalpy of activated complex ($\mathrm{kJ\,mol}^{-1}$)
$k(T)$	rate constant
q	linear rate of heating ($\mathrm{K\,min}^{-1}$)
r^2	correlation coefficient
R	gas constant ($\mathrm{kJ\,mol}^{-1}\,\mathrm{K}^{-1}$)
ΔS^*	entropy of activated complexes ($\mathrm{kJ\,mol}^{-1}\,\mathrm{K}^{-1}$)
t	time (min)
T	absolute temperature (K)
T_m	maximum dehydration rate temperature

Greek letter

α	transformation degree

is often connected in different studies with the various strengths of molecular bonding lost from the initial compound structure: weakly bonded molecules are removed in the early stages, and more strongly bonded ones later. Coordinated and non-coordinated water molecules are stepwise removed from hydrates. The dehydration temperature depends on the strength of the water bonding. Longvinenko [4] says that there is no correlation between the composition and the structure of the intermediate phase and the existence of weakly and strongly bonded water molecules in starting hydrate. The dehydration steps' independence from the starting structure, and the great influence of the equilibrium shift is well known. The entropy term controls the reaction of intermediate hydrate formation.

Many sulphates crystallize with odd numbers of molecules of water of crystallization. Dehydration of these hydrates to the monohydrate stage is easy, but the last molecule of water is not removed until temperatures between 200 and 300 °C are reached.

The present paper reports a kinetic and thermodynamic study of the dehydration of copper, manganese and cadmium hydrated sulphates. The hydrates have a different associated water molecules and crystallised in the various space groups.

The octahedral coordination group around a copper atom in $CuSO_4{\cdot}5H_2O$ is composed of four water molecules and two oxygen atoms of $SO_4{}^{2-}$ ions. The odd water molecule is held by hydroxyl bonds between water molecules coordinated to metal atoms and oxygen atoms of $SO_4{}^{2-}$ ions. In contrast to pentahydrate, in the trihydrate of copper sulphate all water molecules are coordinated to the copper atom. The coordination group around a metal is composed of three water molecules and an oxygen atom of $SO_4{}^{2-}$ ions [1]. Dehydration of this salt was studied by many authors [5–10].

The hydrate cadmium sulphate has a complex structure and contains four crystallographic different groups of water molecules [1]. The decomposition of $3CdSO_4{\cdot}8H_2O$ and properties of its intermediates has been the subject of numerous investigations [11–15].

The rate of a dehydration under non-isothermal conditions has been represented by the relation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)\,f(\alpha) \tag{1}$$

where α is the transformation degree, t the time (min), $k(T)$ is the rate constant, $f(\alpha)$ the conversion function dependent on mechanism of the reaction, and T the absolute temperature (K).

$k(T)$ can be described by the Arrhenius equation:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \tag{2}$$

where R is the gas constant ($\mathrm{kJ\,mol}^{-1}\,\mathrm{K}^{-1}$), E the apparent activation energy ($\mathrm{kJ\,mol}^{-1}$), and A the pre-exponential Arrhenius factor (min^{-1}).

These equations imply a strong correlation between kinetic parameters. The rate constant can also be described by Eyring equation [16]:

$$k(T) = \frac{k_\mathrm{B}T}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) \tag{3}$$

where k_B is the Boltzmann constant, h the Planck's constant, ΔH^* the enthalpy of activated complex ($\mathrm{kJ\,mol}^{-1}$), ΔS^* the entropy of activated complexes ($\mathrm{kJ\,mol}^{-1}\,\mathrm{K}^{-1}$), and ΔG^* the Gibbs free energy of activated complexes ($\mathrm{kJ\,mol}^{-1}$).

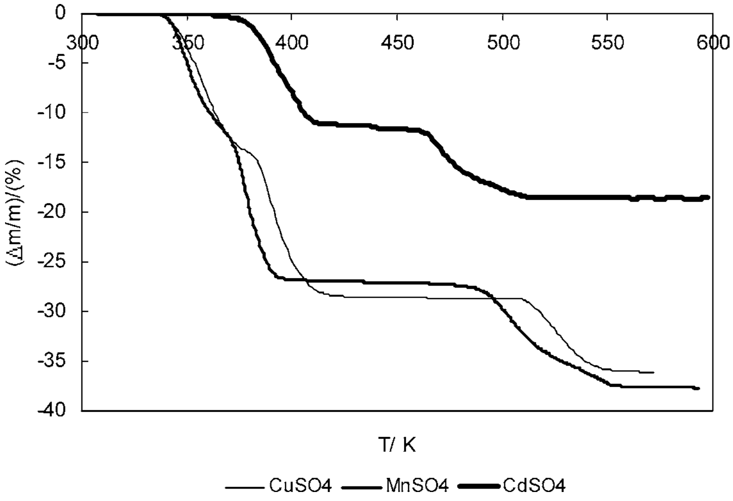

Fig. 1. TG curves for particular hydrated sulphates: $CuSO_4{\cdot}5H_2O$, $MnSO_4{\cdot}5H_2O$ and $3CdSO_4{\cdot}8H_2O$.

After integrating Eq. (1), we have:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^t k(T)\,dt \tag{4}$$

where $g(\alpha)$ is the integral form of conversion function.

In the present study, the kinetics of thermal decomposition of hydrates was followed by integral method by applying the Coats–Redferns approximation:

$$\ln\frac{g(\alpha)}{T^2} = \ln\left[\frac{AR}{qE}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{5}$$

where q is the rate of heating a sample.

A plot of $\ln(g(\alpha)/T^2)$ versus $1/T$ gives a straight line if the model relation is correct.

The thermodynamic functions of activated complexes can be calculated via the equations:

$$\Delta H^* = E - RT \tag{6}$$

$$\Delta S^* = R\left(\ln\frac{hA}{k_B T} - 1\right) \tag{7}$$

$$\Delta G^* = \Delta H^* - T\,\Delta S^* \tag{8}$$

The application of these equations to systems of condensed phases can be justifiable by employing a canonical ensemble approach. From the above equations it seems that the correlation between the enthalpy and entropy of activated complexes will be similar to the correlation between parameters E and $\ln A$.

The correlation coefficient, r^2 and Snedecor's variable, F were calculated to aid the selection of the $g(\alpha)$ function best describing the experimental results.

2. Experimental

These investigations of thermal dehydration of choice hydrated sulphates ($MnSO_4{\cdot}5H_2O$, $CuSO_4{\cdot}5H_2O$ and $3CdSO_4{\cdot}8H_2O$) were carried out in static air atmosphere, at a heating rate of 2–10 K min^{-1}, in the temperature range 293–600 K, with derrivatograph

Table 1
Characteristic parameters of particular dehydration steps of hydrated sulphates at heating rate 10 K min^{-1}

Stage	T_{range} (K)	T_m (K)	Mass loss (%)	
			Found	Theoretical
$MnSO_4{\cdot}5H_2O$				
1	336–370	362.7	12.47	13.07
2	370–399	385.4	26.75	28.01
3	487–530	516.9	35.16	35.48
4	530–556	549.4	37.50	37.34
$CuSO_4{\cdot}5H_2O$				
1	327–380	368.1	14.15	14.42
2	380–421	407.0	28.49	28.84
3	505–553	541.2	35.94	36.05
$3CdSO_4{\cdot}8H_2O$				
1	361–441	404.0	11.54	11.70
2	415–515	496.0	18.58	18.72

Table 2
Kinetic, thermodynamic and statistic parameters of $MnSO_4{\cdot}5H_2O$ thermal dehydration

Model	E (kJ mol^{-1})	A (min^{-1})	r^2	F	ΔS^* (J mol^{-1} K^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})
Stage 1							
D1	162.6	3.16×10^{16}	86.0	312	161.2	159.6	102.7
D2	186.1	6.82×10^{26}	89.2	421	225.0	183.1	103.7
D3	217.8	1.75×10^{31}	92.8	655	309.4	214.9	105.7
D4	196.4	8.98×10^{27}	90.5	488	246.5	193.5	106.5
F1	123.5	1.46×10^{18}	95.2	1006	59.1	120.6	99.8
A2	58.8	2.49×10^{8}	94.7	909	−127.9	55.9	101.0
A3	37.2	1.17×10^{5}	94.1	817	−191.6	34.3	101.9
R1	78.3	1.32×10^{11}	85.0	290	−75.8	75.4	102.1
R2	98.2	1.68×10^{14}	90.7	499	−16.4	95.2	101.0
R3	106.0	2.75×10^{15}	92.4	620	6.9	103.0	100.6
Stage 2							
D1	93.6	2.02×10^{12}	84.1	175	−53.7	90.5	110.9
D2	130.6	2.11×10^{17}	89.8	289	42.4	127.5	111.4
D3	207.0	4.06×10^{27}	97.1	1112	239.3	203.8	112.9
D4	153.5	1.21×10^{20}	92.8	427	95.2	150.3	114.1
F1	153.5	1.23×10^{21}	99.8	18238	114.5	150.3	106.8
A2	73.5	7.33×10^{9}	99.8	16551	−100.4	70.4	108.5
A3	46.9	1.13×10^{6}	99.8	14962	−173.4	43.7	109.6
R1	43.6	2.38×10^{5}	82.1	151	−186.4	40.4	111.2
R2	81.0	6.68×10^{10}	94.1	525	−82.1	77.8	109.0
R3	100.3	3.76×10^{13}	96.9	1041	−29.4	97.1	108.3
Stage 3							
D1	277.5	1.13×10^{28}	94.9	723	245.4	273.3	148.7
D2	314.5	5.14×10^{31}	96.2	988	315.4	310.3	150.1
D3	360.2	1.25×10^{36}	97.5	1510	399.4	355.9	153.1
D4	329.6	6.94×10^{32}	96.7	1138	337.0	325.4	154.2
F1	200.1	2.69×10^{20}	98.3	2281	99.4	195.9	145.4
A2	95.8	3.00×10^{9}	98.2	2086	−110.3	91.6	147.6
A3	61.1	5.68×10^{5}	98.0	1900	−181.5	56.9	149.1
R1	134.5	2.27×10^{13}	94.6	679	−36.0	130.3	148.6
R2	164.6	4.09×10^{16}	96.8	1169	26.3	160.4	147.0
R3	175.9	6.62×10^{17}	97.4	1437	49.5	171.6	146.5
Stage 4							
D1	304.7	7.75×10^{28}	93.2	480	260.8	300.2	158.6
D2	385.0	3.38×10^{36}	96.2	883	407.1	380.5	159.5
D3	517.6	1.16×10^{49}	99.2	4095	647.1	513.1	161.7
D4	426.9	1.48×10^{40}	97.5	1356	476.8	422.4	163.5
F1	334.8	1.92×10^{32}	99.9	128600	325.8	330.3	153.4
A2	162.9	3.01×10^{15}	99.9	121502	4.1	158.3	156.1
A3	105.5	6.34×10^{9}	99.9	114606	−104.6	101.0	157.8
R1	147.8	5.78×10^{13}	92.8	451	−28.8	143.3	158.9
R2	221.5	1.28×10^{21}	98.1	1761	111.8	217.0	156.3
R3	254.3	2.24×10^{24}	99.1	3946	173.9	249.8	155.3

MOM-PC (Hungary). All hydrates used in the present study after recrystallization from water were an analytical grade materials and were supplied by PPH Polskie Odczynniki Chemiczne, Gliwice, Poland. The sample mass was 20 mg.

3. Results and discussion

The thermal decomposition of particular analysed hydrates is characterised by several stages. The changes in the TG run at 10 K min^{-1} are shown in

Table 3
Kinetic, thermodynamic and statistic parameters of $CuSO_4 \cdot 5H_2O$ thermal dehydration

Model	E (kJ mol^{-1})	A (min^{-1})	r^2	F	ΔS^* (J mol^{-1} K^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})
Stage 1							
D1	120.4	9.89×10^{16}	92.7	291	36.5	117.4	104.3
D2	144.5	2.47×10^{20}	95.5	484	101.6	141.5	105.0
D3	179.9	1.96×10^{25}	98.2	1272	195.4	176.9	106.7
D4	155.9	4.49×10^{21}	96.6	652	125.7	152.9	107.8
F1	107.2	3.38×10^{15}	99.5	4533	8.5	104.2	101.2
A2	50.6	1.10×10^{7}	99.4	3990	−154.0	47.6	102.9
A3	31.7	1.40×10^{4}	99.3	3488	−209.4	28.7	103.9
R1	57.2	6.30×10^{7}	91.9	262	−139.5	54.2	104.3
R2	78.2	1.19×10^{11}	96.9	728	−76.8	75.2	102.8
R3	86.9	2.62×10^{12}	98.1	1183	−51.1	83.9	102.3
Stage 2							
D1	105.4	1.77×10^{13}	79.8	111	−35.9	102.2	116.2
D2	131.5	3.98×10^{16}	85.3	162	28.3	128.3	117.3
D3	175.9	1.74×10^{22}	92.4	339	136.3	172.7	119.5
D4	145.4	1.11×10^{18}	88.0	205	56.0	142.2	120.4
F1	112.1	4.62×10^{14}	96.6	788	8.8	108.9	112.3
A2	52.7	3.76×10^{6}	96.1	693	−163.6	49.5	113.3
A3	32.9	7.02×10^{3}	95.6	604	−216.6	29.7	114.1
R1	49.4	7.15×10^{5}	77.6	97	−177.4	46.1	115.3
R2	73.6	1.99×10^{9}	88.6	218	−111.5	70.4	113.8
R3	84.6	6.94×10^{10}	91.8	313	−82.0	81.4	113.3
Stage 3							
D1	182.3	1.98×10^{17}	84.6	176	39.2	178.0	157.5
D2	227.9	4.97×10^{21}	89.6	275	123.5	223.5	159.2
D3	307.7	2.29×10^{29}	95.9	748	270.2	303.4	162.6
D4	252.6	5.58×10^{23}	92.1	371	162.7	248.3	163.5
F1	200.6	4.40×10^{19}	98.9	2964	84.1	196.3	152.5
A2	95.9	1.15×10^{9}	98.8	2691	−118.5	91.5	153.3
A3	60.9	2.89×10^{5}	98.7	2433	−187.4	56.6	154.2
R1	86.7	7.38×10^{7}	83.3	159	−141.3	82.4	156.0
R2	129.5	2.18×10^{12}	93.0	425	−55.7	125.2	154.2
R3	149.4	2.48×10^{14}	95.7	704	−16.3	145.1	153.6

Fig. 1. The values of characteristic parameters of dehydration processes are presented in Table 1.

Analysis of the weight losses changes suggests the following scheme for the dehydration processes of analysed compounds:

For $MnSO_4 \cdot 5H_2O$:

1. $MnSO_4 \cdot 5H_2O \rightarrow MnSO_4 \cdot 3.25H_2O + 1.75H_2O$;
2. $MnSO_4 \cdot 3.25H_2O \rightarrow MnSO_4 \cdot 1.25H_2O + 2H_2O$;
3. $MnSO_4 \cdot 1.25H_2O \rightarrow MnSO_4 \cdot 0.25H_2O + H_2O$;
4. $MnSO_4 \cdot 0.25H_2O \rightarrow MnSO_4 + 0.25H_2O$.

For $CuSO_4 \cdot 5H_2O$:

1. $CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot 3H_2O + 2H_2O$;
2. $CuSO_4 \cdot 3H_2O \rightarrow CuSO_4 \cdot H_2O + 2H_2O$;
3. $CuSO_4 \cdot H_2O \rightarrow CuSO_4 + H_2O$.

For $3CdSO_4 \cdot 8H_2O$:

1. $3CdSO_4 \cdot 8H_2O \rightarrow 3CdSO_4 \cdot H_2O + 5H_2O$;
2. $CdSO_4 \cdot H_2O \rightarrow CdSO_4 + H_2O$.

The dehydration steps of $3CdSO_4 \cdot 8H_2O$ under experimental conditions are not at all connected with this different bonding of the water molecules; there is no step of loss for the two weakly bonded uncoordinated water molecules. This hydrate decomposes with the formation of only one stable phase—monohydrate.

Decompositions of the all examined hydrates were endothermic processes. The variable α was calculated from the fractional mass loss (TG).

Table 4
Kinetic, thermodynamic and statistic parameters of $3CdSO_4{\cdot}8H_2O$ thermal dehydration

Model	E (kJ mol^{-1})	A (min^{-1})	r^2	F	ΔS^* (J mol^{-1} K^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})
Stage 1							
D1	217.3	1.54×10^{28}	91.3	87	249.9	214.0	114.2
D2	240.1	1.19×10^{31}	93.9	570	305.2	236.8	115.1
D3	273.2	1.51×10^{35}	96.9	1169	383.8	269.8	116.7
D4	250.7	1.17×10^{32}	95.0	709	324.2	247.4	118.1
F1	152.5	1.26×10^{20}	98.7	2886	95.1	149.2	111.3
A2	73.0	2.31×10^{9}	98.6	2622	−110.4	69.7	113.7
A3	46.5	5.18×10^{5}	98.5	32373	−180.3	43.2	115.1
R1	105.4	3.03×10^{13}	90.8	364	−31.6	102.1	114.7
R2	125.1	1.85×10^{16}	95.4	771	21.7	121.8	113.2
R3	133.3	2.59×10^{17}	96.8	1110	43.7	130.0	112.6
Stage 2							
D1	267.7	1.41×10^{28}	85.2	386	247.7	263.8	146.1
D2	288.1	1.66×10^{30}	87.6	473	287.4	284.2	147.7
D3	317.6	1.40×10^{33}	90.9	672	343.4	313.6	150.5
D4	297.6	6.82×10^{30}	88.7	528	299.1	293.6	151.5
F1	172.0	2.22×10^{18}	93.6	981	60.1	168.1	139.5
A2	82.0	2.69×10^{8}	93.0	888	−129.8	78.1	139.7
A3	52.0	1.13×10^{5}	92.3	800	−194.4	48.1	140.4
R1	129.9	2.63×10^{13}	84.4	363	−34.2	125.9	142.2
R2	147.5	3.10×10^{15}	88.9	535	5.4	143.6	141.0
R3	154.8	2.21×10^{16}	90.5	637	21.8	150.9	140.5

The α–temperature curves from non-isothermal TG experiments were used to determine the mechanism of the individual stages and were fitted by well-known kinetic models [16]. The values of kinetic and thermodynamic parameters obtained at heating rate 10 K min^{-1} from different $g(\alpha)$ functions for particular stages of analysed hydrates are shown in Tables 2–4.

The best model was chosen at heating rate 10 K min^{-1} on the basis of statistic parameters values—r^2 and F. From Tables 2–4, it can be seen that the most suitable expressions for the all dehydration stages are those of the random nucleation model F1 over the widest α range and an activation energies for this model were in the range from 107 (the first stage for $CuSO_4{\cdot}5H_2O$) to 335 kJ mol^{-1} (the last stage for $MnSO_4{\cdot}5H_2O$). The highest values of E for the last dehydration stages reflect the fact that the final water molecule is most strongly bound. The hydrates: $MnSO_4{\cdot}5H_2O$ and $CuSO_4{\cdot}5H_2O$ decompose at approximately equal temperatures, have approximately equal values of Gibbs energies of activated complexes but the entropy term contribution is higher in the case of $MnSO_4{\cdot}5H_2O$.

The dependencies of the enthalpy of activation on the entropy of transient state for different kinetic models are shown in Figs. 2–4 and can be described as follows:

Stage	ΔH^*	r^2
$MnSO_4{\cdot}5H_2O$		
1	$362.4\,\Delta S^* + 101.9$	0.9994
2	$385.4\,\Delta S^* + 110.3$	0.9984
3	$516.9\,\Delta S^* + 148.0$	0.9996
4	$549.4\,\Delta S^* + 156.7$	0.9996
$CuSO_4{\cdot}5H_2O$		
1	$368.1\,\Delta S^* + 104.3$	0.9989
2	$407.0\,\Delta S^* + 116.5$	0.9982
3	$541.0\,\Delta S^* + 156.3$	0.9989
$3CdSO_4{\cdot}8H_2O$		
1	$404.0\,\Delta S^* + 113.9$	0.9995
2	$496.5\,\Delta S^* + 142.0$	0.9995

Table 5 lists the kinetic and thermodynamic parameters for dehydration of all analysed salts at dif-

Table 5
Characteristic parameters of dehydration at different heating rates (F1 model)

β (K min^{-1})	E (kJ mol^{-1})	ln A (min^{-1})	T_{max} (K)	ΔS^* (J mol^{-1} K^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})
$MnSO_4$						
Stage 1						
2.5	186.2	65.5	334	256.3	183.5	97.9
5	166.5	57.8	342	192.0	163.7	98.0
7.5	144.7	49.8	346	125.4	141.8	98.5
10	123.5	41.8	353	59.1	120.6	99.8
Stage 2						
2.5	238.6	78.1	361	360.7	235.6	105.3
5	212.3	69.0	363	285.2	209.3	105.8
7.5	189.6	60.6	374	214.9	186.5	106.1
10	153.5	48.6	380	114.5	150.3	106.8
Stage 3						
2.5	293.0	70.9	486	298.1	289.0	144.2
5	261.8	62.7	491	230.1	257.8	144.7
7.5	230.6	54.0	519	157.1	226.3	144.8
10	200.1	47.0	508	99.4	195.9	145.4
Stage 4						
2.5	381.8	87.2	523	432.9	377.4	150.8
5	379.9	85.8	532	421.5	375.5	151.5
7.5	357.0	80.0	536	373.0	352.5	152.5
10	334.8	74.3	543	325.8	330.3	153.4
$CuSO_4$						
Stage 1						
2.5	162.6	55.9	347	176.3	159.7	98.6
5	150.3	51.2	351	136.8	147.4	99.4
7.5	128.0	42.8	359	66.8	125.1	101.1
10	107.2	35.8	359	8.5	104.2	101.2
Stage 2						
2.5	217.7	69.0	373	284.9	214.6	108.4
5	183.0	57.2	379	186.6	179.9	109.1
7.5	150.0	46.0	387	93.1	146.7	110.8
10	112.1	33.8	390	−8.8	108.9	112.3
Stage 3						
2.5	248.5	58.2	498	192.3	244.4	148.6
5	234.3	54.4	506	160.4	230.0	148.8
7.5	213.6	49.1	515	116.4	209.3	149.4
10	200.6	45.2	521	84.1	196.3	152.5
$CdSO_4$						
Stage 1						
2.5	166.7	53.2	354	153.7	163.8	109.3
5	162.8	51.0	362	135.5	159.7	110.7
7.5	159.9	49.8	369	125.1	156.8	110.6
10	152.5	46.3	399	95.1	149.2	111.3
Stage 2						
2.5	219.0	57.0	431	183.2	215.4	136.4
5	206.4	52.8	443	148.2	202.7	137.0
7.5	192.8	48.8	440	115.0	189.2	138.5
10	172.0	42.2	475	60.1	168.1	139.5

Table 5 (*Continued*)

β (K min^{-1})	E (kJ mol^{-1})	ln A (min^{-1})	T_{max} (K)	ΔS^* (J mol^{-1} K^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})
$CdSO_4$						
Stage 1						
2.5	166.7	53.2	354	153.7	163.8	109.3
5	162.8	51.0	362	135.5	159.7	110.7
7.5	159.9	49.8	369	125.1	156.8	110.6
10	152.5	46.3	399	95.1	149.2	111.3
Stage 2						
2.5	219.0	57.0	431	183.2	215.4	136.4
5	206.4	52.8	443	148.2	202.7	137.0
7.5	192.8	48.8	440	115.0	189.2	138.5
10	172.0	42.2	475	60.1	168.1	139.5

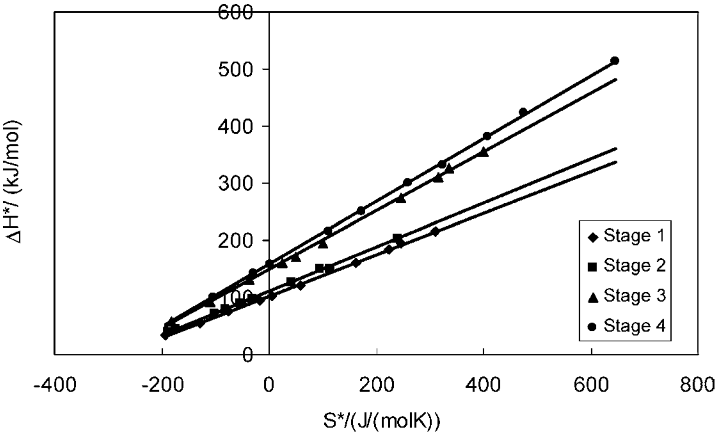

Fig. 2. Dependence between the enthalpy and entropy of activated complexes created in thermal dehydration of $MnSO_4 \cdot 5H_2O$.

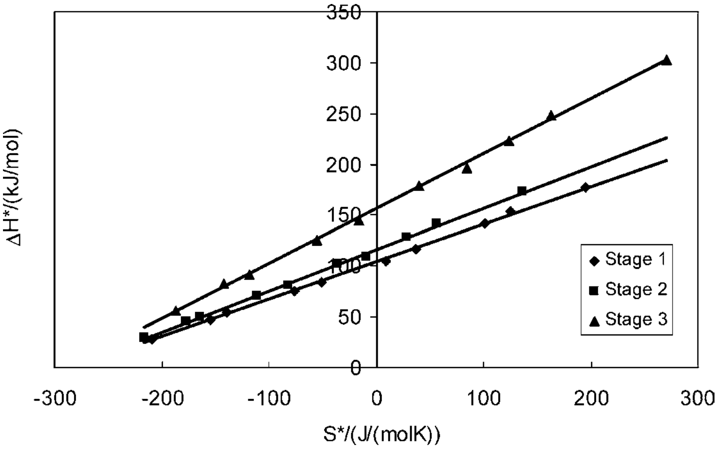

Fig. 3. Dependence between the enthalpy and entropy of activated complexes created in thermal dehydration of $CuSO_4 \cdot 5H_2O$.

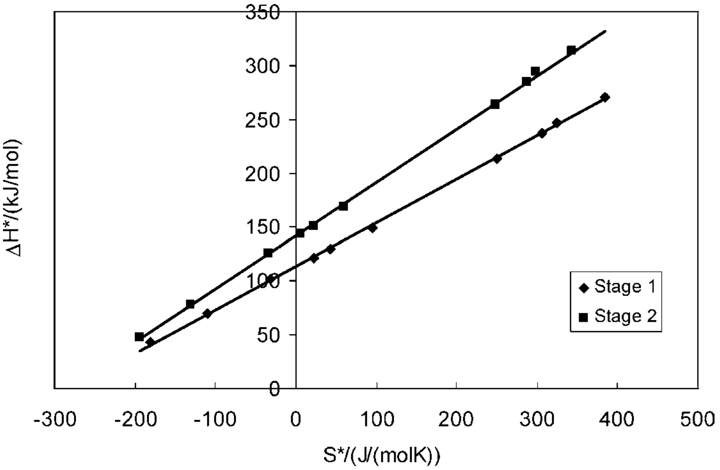

Fig. 4. Dependence between the enthalpy and entropy of activated complexes created in thermal dehydration of $3CdSO_4{\cdot}8H_2O$.

ferent heating rates (F1 model). From these data it seems that the apparent kinetic energies, the logarithm of pre-exponential factor, the enthalpy and the entropy for the particular steps of dehydration decrease with a rise in heating rate. The maximum dehydration rate temperature and the Gibbs free energy of activated complexes increase with a rise in heating rate.

Figs. 5 and 6 show the example dependencies of ΔS^* and ΔH^* on heating rates for dehydration of manganese sulphate.

Table 6 lists the characteristic parameters values of dehydration which were calculated by an extrapolation of functions and $T_{\max}$, respectively, at zero heating rate (under isothermal conditions).

The dependence of Gibbs free energy of activated complexes calculated for F1 model on the maximum dehydration rate temperature can be described by equation

$$\Delta G^* = 0.29\,T_{\rm m} - 0.4697 \qquad r^2 = 0.963$$

and is shown in Fig. 7.

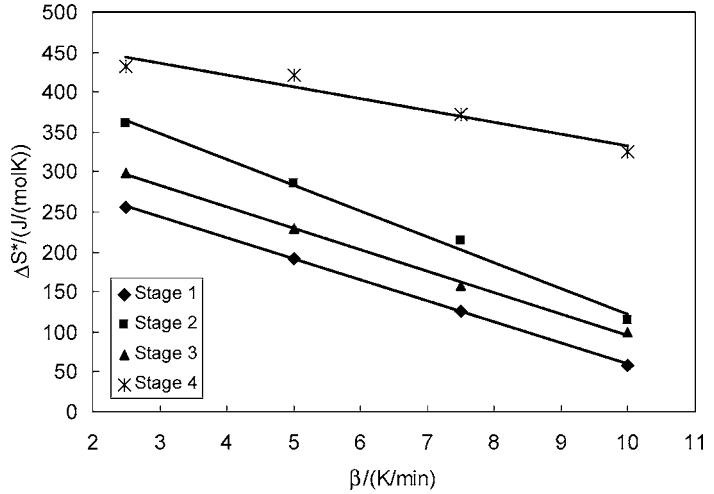

Fig. 5. Correlation between the entropy of activated complexes and the heating rate for $MnSO_4$.

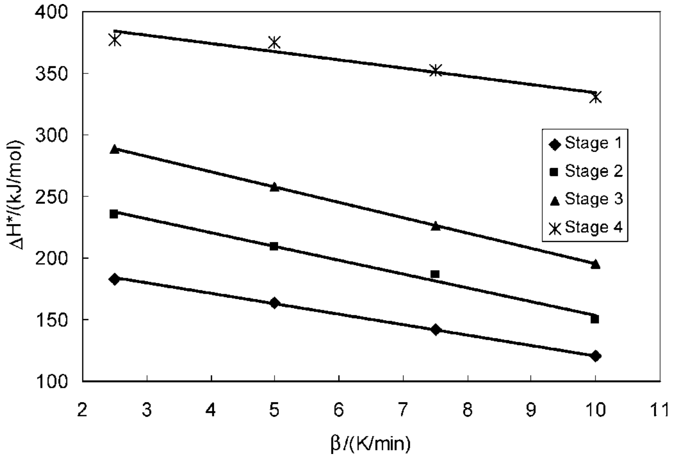

Fig. 6. Correlation between the enthalpy of activated complexes and the heating rate for $MnSO_4$.

Table 6
Extrapolated values of characteristic parameters of dehydration

Stage	E_0 (kJ mol^{-1})	$\ln A_0$ (min^{-1})	$T_{0\,\max}$ (K)	ΔS_0^* (J mol^{-1} K^{-1})	ΔH_0^* (kJ mol^{-1})	ΔG_0^* (kJ mol^{-1})
$MnSO_4$						
1	207.7	73.5	328.5	322.7	205.0	99.0
2	268.0	88.4	352.8	446.0	265.1	107.7
3	323.9	78.7	477.4	363.5	319.9	146.4
4	404.3	92.9	517.7	480.8	400.0	151.1
$CuSO_4$						
1	184.2	63.6	342.4	240.5	181.3	99.0
2	253.2	80.8	367.4	382.5	250.1	109.6
3	265.3	62.8	490.7	230.4	261.3	148.2
$CdSO_4$						
1	171.8	55.6	335.7	174.0	169.0	110.7
2	236.2	62.2	415.3	227.2	232.7	138.4

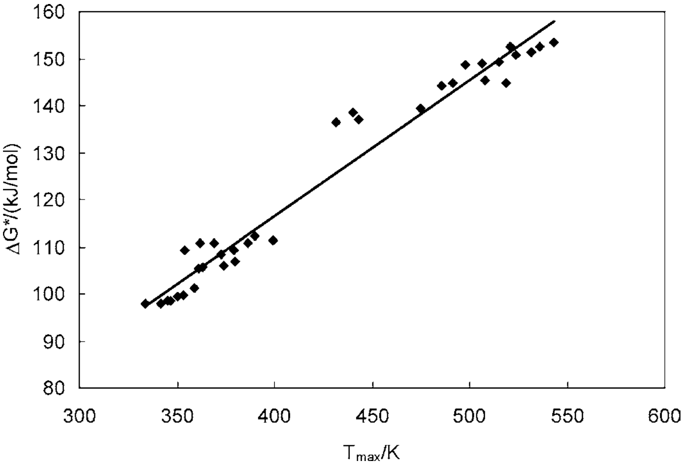

Fig. 7. Correlation between the Gibbs free energy of activated complexes and the maximum dehydration rate temperature.

4. Conclusion

The course of thermal dehydration of all salts investigated under experimental conditions in this study can be described by the F1 kinetic model.

This work supports the claim that the different bonding of water molecules in the structure of starting hydrates is not always reflected in stepwise character of thermal dissociation. All these investigated hydrates had fewer stages of thermal dehydration than the various bonding water molecules.

The apparent kinetic energies, the logarithm of pre-exponential factor, the enthalpy and the entropy for the particular steps of dehydration decrease with a rise in heating rate. The maximum dehydration rate temperature and the Gibbs free energy of activated complexes increase with a rise in heating rate.

The Gibbs free energy of activated complexes formed in investigating thermal dehydration processes is the lineal function of the maximum dehydration rate temperature.

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