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Kinetics of thermal decomposition of $ZnSO_4 \cdot 7H_2O$

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Abstract

The thermal decomposition of $ZnSO_4 \cdot 7H_2O$ was studied under non-isothermal conditions in air. The kinetics of particular stages of $ZnSO_4 \cdot 7H_2O$ decomposition were evaluated from the dynamic weight losses data by means of integral method. The values of the activation energy E, and the preexponential factor A of each stage of the thermal decomposition were calculated. © 1997 Elsevier Science B.V.

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1. Introduction

The thermal decomposition of zinc sulphate and the kinetics of the process have been studied as a part of the programme to investigate the thermal dissociation of metal sulphates of the fourth period of Mendeleev's classification. In addition to academic interest they have always played an important role in metallurgy. Zinc sulphate can be formed as an intermediate product during the calcination process of zinc ore.

A number of papers have reported on the many stages in the pyrolysis of hydrated zinc sulphate; however, the mechanism of these reactions and the kinetic parameters of the processes have not been described unequivocally.

The aim of the present work is to obtain more detailed information on the thermal decomposition of $ZnSO_4 \cdot 7H_2O$, to fit kinetic models and to estimate kinetic parameters.

The rate of a reaction under non-isothermal conditions has been expressed by the relation [1]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where α represents the transformation degree at time t, $f(\alpha)$ the conversion function dependent on mechanism of the reaction, and $k(T)$ the rate constant as a function of temperature. After integrating Eq. (1), we have:

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^t k\,dt \tag{2}$$

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

$$k(T) = A\exp\left(-\frac{E}{RT}\right) \tag{3}$$

where A is the preexponential factor, E the activation energy, and R the gas constant or, by an equation of the Eyring type:

$$k(T) = \frac{k_B T}{h}\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(-\frac{\Delta H^*}{RT}\right) \tag{4}$$

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where k_B is the Boltzmann constant, h the Planck constant, ΔS^* the entropy of activation, and ΔH^* the enthalpy of activation or, of the Wertera and Zenera type:

$$k(T) = \nu \exp\left(-\frac{\Delta G^*}{RT}\right) \qquad (5)$$

where ν is the Einstein vibration frequency, and ΔG^* the free energy of activation.

In the present study, the kinetics of thermal decomposition of $ZnSO_4 \cdot 7H_2O$ was followed by the integral method by applying the Coats–Redferns approximation:

$$\ln\frac{g(\alpha)}{T^2} = \ln\left[\frac{AR}{qE}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad (6)$$

where q is the linear heating rate. This equation is frequently used to describe the kinetics of thermal decomposition of solids in general. A plot of $\ln[g(\alpha)/T^2]$ vs. $1/T$ gives a straight line if the model relation is correct.

The algebraic expression of integral $g(\alpha)$ functions for the most common mechanism used in kinetics of solid-state decomposition tested in this work are listed in Table 1.

The following parameters were calculated to aid the selections of the $g(\alpha)$ function which best describes the experimental results:

1. the correlation coefficient (r)
2. standard error of estimation (s)
3. Snedecor's variable (F).

The confidence interval of free energy of activation, ΔG^*, has been calculated. The confidence limit was 95%.

2. Experimental

The crystalline salt $ZnSO_4 \cdot 7H_2O$ used in the present investigation was of an analytical grade (P.P.H. Polskie Odczynniki Chemiczne Gliwice, Poland). The thermogravimetric measurements were carried out on the Hungarian derivatograph MOM 1500. The operational characteristics are as follows:

- heating rate: 5 K $\min^{-1}$
- sample size: 700 mg
- atmosphere: static air
- temperature range: 20–1000°C

Seven experiments were carried out under the same conditions. The reproducibility was good.

3. Results

The thermal analysis curves of the zinc sulphate heptahydrate (Fig. 1) show several peaks. The weight decreased was stabilized at ~900°C. The TG curve for this salt show six temperature regions in which there are weight losses with maximum rate at 89, 111, 212, 267, 782, and 861°C in the DTG curve. The DTA curve shows that the first step of decomposition complex is that B, the most intense, appeared to be

Table 1
Kinetic model investigated

Model	$g(\alpha)$	Macromechanism
D1	α^2	One-dimensional diffusion (power law)
D2	$(1-\alpha)\ln(1-\alpha)+\alpha$	Two-dimensional diffusion; cylindrical symmetry
D3	$3/2[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion; spherical symmetry, Jander equation
D4	$3/2[1-2\alpha/3-(1-\alpha)^{2/3}]$	Three-dimensional diffusion; spherical symmetry, Ginstling– Brounshtein equation
F1	$[-\ln(1-\alpha)]$	Random nucleation; only one nucleus on each particle
A2	$[-\ln(1-\alpha)]^{1/2}$	Random nucleation; Avrami I equation
A3	$[-\ln(1-\alpha)]^{1/3}$	Random nucleation; Avrami II equation
R1	α	Phase boundary reaction (zero order); Polanyi–Wigner equation
R2	$2[1-(1-\alpha)^{1/2}]$	Phase boundary reaction; cylindrical symmetry
R3	$3[1-(1-\alpha)^{1/3}]$	Phase boundary reaction; spherical symmetry

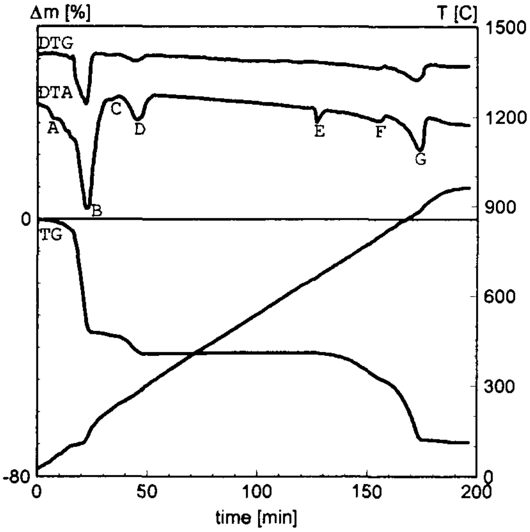


Fig. 1. Thermoanalytical curves of thermal decomposition of $ZnSO_4 \cdot 7H_2O$ in air.

composed of three overlapping peaks and several dehydration reactions occur simultaneously. Other DTA peaks were distinct. All the peaks were associated with endothermic processes. Peaks A–D, F and G were associated with weight losses, while peak E showed no change in weight, typical of a phase transition. Peak A was accompanied by a weight loss of 5.25%, corresponding to the release of 1 mol of water. Peak B was associated with a total weight loss of 31.07% which was equivalent to the removal of 5 mol of water per mole of $ZnSO_4$. Peak C represents further dehydration. The weight loss in this stage was ~0.86%. Most investigators did not detect this peak in their study [2–6]. The last part of water was removed at 232–277°C during the appearance of peak D.

Two allotropes of $ZnSO_4$ were identified with characteristic phase transition in their DTA curve. The small peak E of anhydrous $ZnSO_4$ represents a transition from H-$ZnSO_4$ to N-$ZnSO_4$. This is in agreement with the previous opinion [2].

One peak F is associated with the formation of the basic salt $ZnO \cdot 2ZnSO_4$ and corresponds to a weight loss of 8.46%. The decomposition of this salt also began at ~807°C. ZnO, the last product of thermal dissociation, is formed during the appearance of peak G.

On the basis of this study, we find that the following reactions occur in the course of the thermal decomposition of $ZnSO_4 \cdot 7H_2O$:

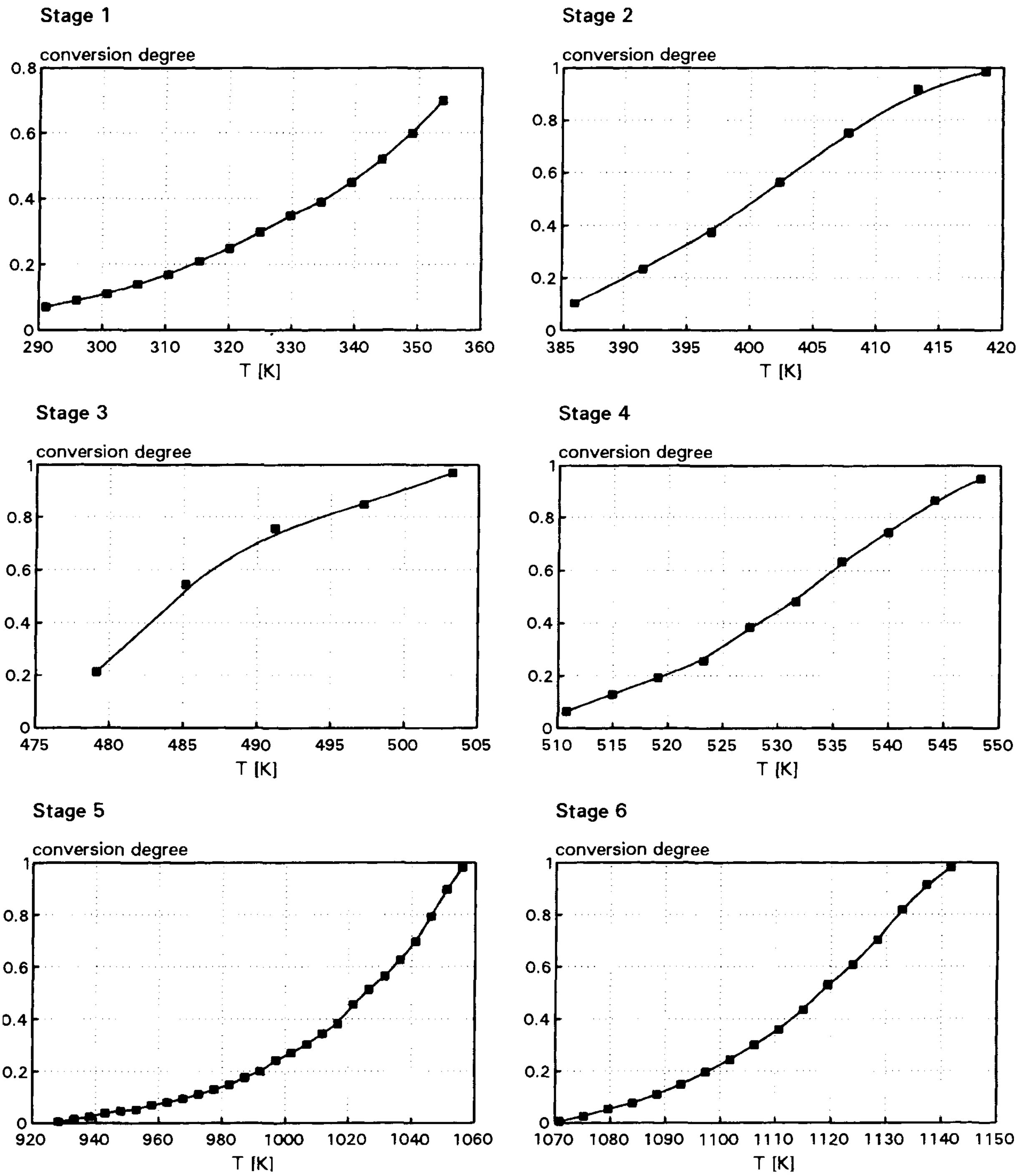
1. $ZnSO_4 \cdot 7H_2O \rightarrow ZnSO_4 \cdot 6H_2O + H_2O$
2. $ZnSO_4 \cdot 6H_2O \rightarrow ZnSO_4 \cdot H_2O + 5H_2O$
3. $ZnSO_4 \cdot H_2O \rightarrow ZnSO_4 \cdot xH_2O + (1-x)H_2O$, where $x = 0.8$–0.9
4. $ZnSO_4 \cdot xH_2O \rightarrow ZnSO_4 + xH_2O$
5. $3ZnSO_4 \rightarrow ZnO \cdot 2ZnSO_4 + SO_3$
6. $ZnO \cdot 2ZnSO_4 \rightarrow 3ZnO + 2SO_3$

The thermal stability sequence was in a good agreement with the Spiess results [2]. The thermal characteristic of each reaction studied are summarized in Table 2.

From the mass loss – temperature dependence observed in the TG-curves, the α–T relations for the particular steps were estimated. Based on the $\alpha(T)$ dependences (Fig. 2), the $g(\alpha)$ function from well-known models (Table 1), which best described the experimental results of the decomposition, were chosen. Average values of the apparent activation energy E, preexponential factor A, linear regression coefficient r, Snedecor's variable F, the standard error of estimation s, entropy, enthalpy, free energy of activa-

Table 2
Thermal analysis data of $ZnSO_4 \cdot 7H_2O$

Stage	Temperature range/(K)	DTG peak temperature/(K)	Mass loss/(%)	
			experimental	theoretical
1	293–380	362	5.25	6.26
2	375–460	384	31.07	31.30
3	470–505	485	0.86	6.26
4	505–550	540	5.21	
5	925–1085	1055	8.46	9.25
6	1080–1170	1134	18.57	18.59



Stage 1

Stage 2

Stage 3

Stage 4

Stage 5

Stage 6

Fig. 2. Variation of conversion degree with temperature for different stages of decomposition of $ZnSO_4 \cdot 7H_2O$ in air.

tion and confidence interval of free energy of activation obtained from analysis of seven dynamic TG curves on the basis of Eq. (6), are listed in Table 3. The values in Table 3 were obtained from those tested equations which best fit the experimental TG curves.

From Table 3, it can be seen that the best fit for the first stage of $ZnSO_4 \cdot 7H_2O$ dehydration is diffusion D1 model with an activation energy of 55 kJ mol^{-1}. This is a typical value for a dehydration process. The remaining stages of dehydration were described by a random nucleation F1 model, with activation energies increasing from 138 to 224 kJ mol^{-1}. The higher values of E and A for peaks C and D reflect the latter water molecules being more strongly bound.

The decomposition of anhydrous zinc sulphate to basic salt is controlled by a random nucleation F1 model too. The experimental results of decomposition of the basic salt confirm the fact, that in some cases it is impossible to choose one kinetic model from dynamic measurements. This step of decomposition is governed by the three-dimensional diffusion model D3 or the contracting volume model R3. Our results for this stage of decomposition are different from those presented in the literature [5,6].

Table 3
Kinetic and statistical parameters values from dynamic TG experiments

Stage	Model	E (kJ mol^{-1})	A (min^{-1})	Statistical parameters			ΔH^* (kJ mol^{-1})	ΔS^* (J mol^{-1})	ΔG^* (kJ mol^{-1})	Confidence interval of ΔG^* /(%)
				r	s	F				
1	D1	55	1.84×10^{7}	0.9962	0.109	3277	52	−150	106	1.6
2	F1	139	4.43×10^{17}	0.9974	0.096	944	135	48	117	2.4
3	F1	200	1.32×10^{21}	0.9857	0.272	49	196	113	141	1.1
4	F1	224	2.98×10^{21}	0.9922	0.169	1259	220	119	156	0.8
5	F1	261	2.18×10^{12}	0.9985	0.056	6140	252	−62	319	2.4
6	D3	1085	1.42×10^{49}	0.9991	0.083	5731	1075	643	348	2.9
	R3	533	$1.17\times.10^{24}$	0.9991	0.041	5537	524	162	340	1.5

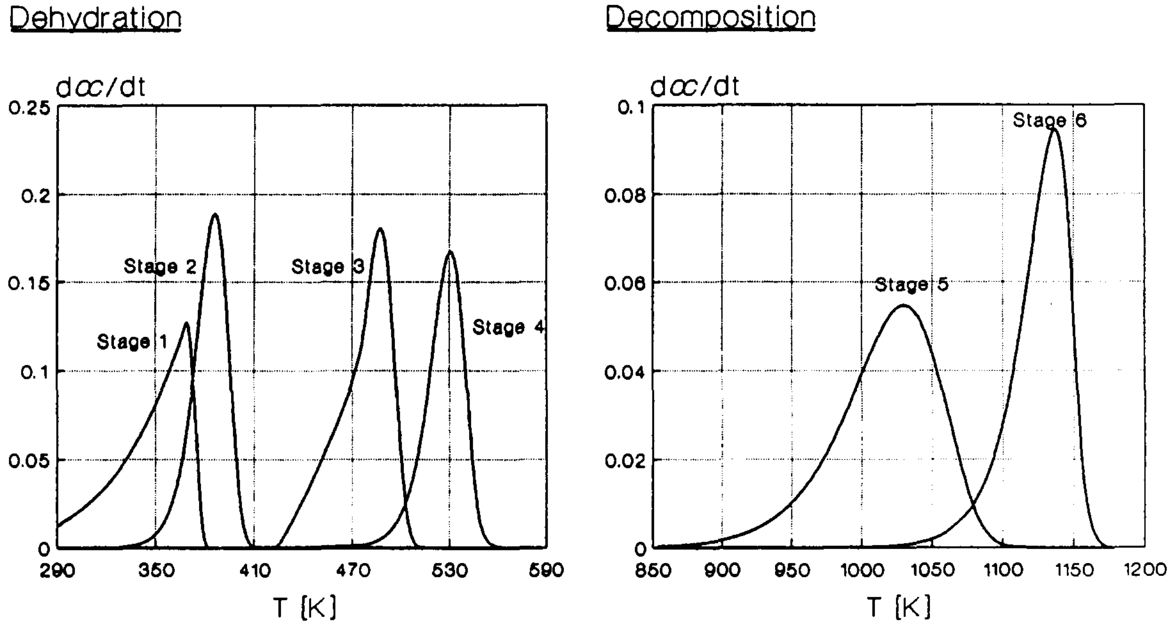


Fig. 3. Variation of reaction rates with temperature for different stages of decomposition of $ZnSO_4 \cdot 7H_2O$ in air.

The dependences of reaction rates on temperature for particular stages of decomposition, calculated from the derived kinetic equations, are presented in Fig. 3. It appears that the double peaks relate to the intermediate products (mesophases) in the thermal decomposition.

4. Conclusions

The thermal decomposition of the zinc sulphate heptahydrate occurs in six steps. The elimination of water takes place at temperatures below 277°C in four stages. The first step of dehydration is governed by diffusion, the remaining steps by nucleation. The activation energy of the dehydration processes increases with decreasing hydration number of the zinc from 55 to 224 kJ mol^{-1}.

Anhydrous zinc sulphate forms at 277°C and the phase transition *H*-$ZnSO_4$ in *N*-$ZnSO_4$ takes place at ~657°C.

The decomposition of anhydrous zinc sulphate occurs in two stages. In the first, the basic salt $ZnO{\cdot}2ZnSO_4$ is formed at 780°C. The kinetics of this process is controlled by the nucleation model F1. The last step of decomposition is the formation of ZnO and takes place at 861°C. It can be described either by a three-dimensional diffusion model D3 or a contracting volume model R3. These stages have a high activation energy, the first 260 kJ mol^{-1} and the second 1100 kJ mol^{-1} for D3 model or 530 kJ mol^{-1} for R3 model, respectively.

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