

THE KINETIC PARAMETERS OF THERMAL DECOMPOSITION HYDRATED IRON SULPHATE

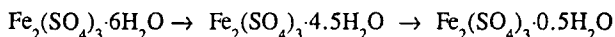
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Abstract

The thermal decomposition of iron sulphate hexahydrate was studied by thermogravimetry at a heating rate of $5^{\circ}\text{C min}^{-1}$ in static air. The kinetic parameters were evaluated using the integral method by applying the Coats and Redfern approximation. The thermal stabilities of the hydrates were found to vary in the order.



The dehydration process of hydrated iron sulphate was found to conform to random nucleation mass loss kinetics, and the activation energies of the respective hydrates were 89.82, 105.04 and $172.62 \text{ kJ mol}^{-1}$, respectively. The decomposition process of anhydrous iron sulphate occurs in the temperature region between 810 and 960 K with activation energies $526.52 \text{ kJ mol}^{-1}$ for the D3 model or $256.05 \text{ kJ mol}^{-1}$ for the R3 model.

Keywords: hydrated iron sulphate, kinetics parameters

Introduction

The important applications of iron(III) sulphate hydrates and Fe_2O_3 are well known. The kinetics of the decomposition of sulphate hydrates has been studied owing to their technical importance and theoretical interest. Several studies of the thermal behaviour of these compounds have been carried out [1] but they did not describe the compositions of decomposition intermediates and the kinetic equations. The application of TG, DTG and DTA in a static atmosphere to study these decompositions has also been described [2-4], but the activation energy and preexponential factor data determined are different.

The aim of the present work was to obtain more detailed information on the decomposition of iron sulphate hexahydrate and the possible existence of intermediates and to calculate the kinetic parameters of all stages of decomposition.

Experimental

The TG, DTG and DTA curves were obtained using a derivatograph, type 1500 (MOM, Hungary) in static air in the temperature range $25-1000^{\circ}\text{C}$ at a heating rate of $5^{\circ}\text{C min}^{-1}$. Sample mass was 700 mg.

The $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ (chemically pure) used in this study was supplied by PPH Polskie Odczynniki Chemiczne Gliwice, Poland.

The reproducibility was good.

Results and discussion

The thermoanalytical curves (TG, DTG, DTA) of $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ are shown in Fig. 1 and the analysis data are summarized in Table 1. The TG curve shows a continuous mass loss around 330–500 K indicating that the sulphate hydrates formed at this temperature are unstable in the study conditions. The DTG and DTA curves exhibit three endothermic steps of dehydration. The first, between 330–430 K is generally interpreted as being caused by the loss of 1.5 mol of water (mass loss of 5.61%, theoretically 5.31%). In the second stage 4 moles of crystal water are lost

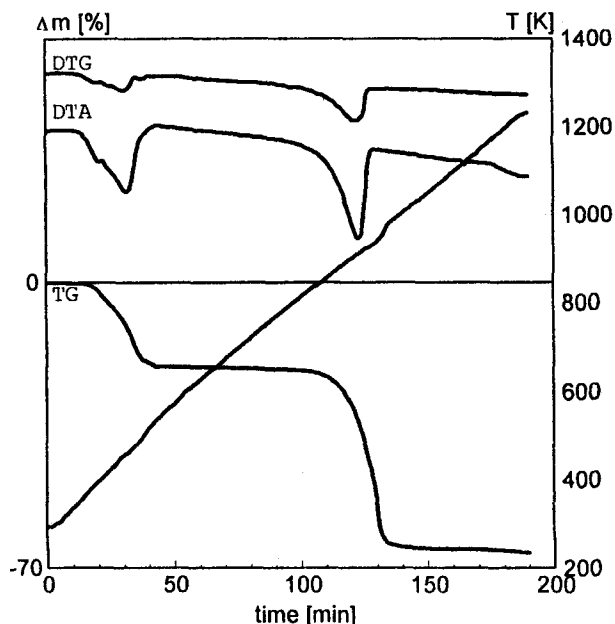


Fig. 1 Thermoanalytical curves of thermal decomposition of $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ in air

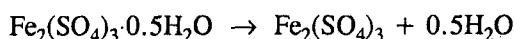
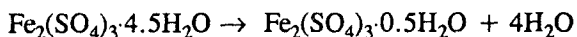
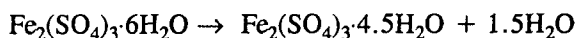
Table 1 Thermal analysis data of $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$

Stage	$T_{\text{range}}/\text{K}$	$T_{\text{DTG peak}}/\text{K}$	Mass loss/ %	
			found	theoret.
1	330–430	415	5.63	5.31
2	430–500	478	13.60	14.18
3	500–542	537	1.76	1.77
4	810–960	947	46.36	47.29

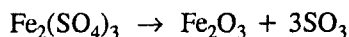
between 430–500 K and in the third step the last 0.5 mole of water is removed. The three steps are associated with a total mass loss of 21%. The weight is stabilized at about 500 K where anhydrous $\text{Fe}_2(\text{SO}_4)_3$ is formed. Finally, between 810 and 960 K a separate step connected with the formation of Fe_2O_3 was detected, with a mass loss of 46.36%.

On the basis of our study the following reactions were assumed to occur in the course of the thermal decomposition of $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$:

Dehydration



Decomposition of anhydrous iron sulphate



From the mass losses observed in the TG-curves the α -T relations were estimated for the individual steps. Kinetic analysis of experimental TG-curves recorded under non-isothermal conditions was carried out by means of an integral method by applying the Coats and Redfern equation because it has been found to yield the best results [5]:

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

where α represents the conversion degree, $g(\alpha)$ is the conversion function which depends on the mechanism of reaction, T – is the absolute temperature, A – is the pre-exponential Arrhenius factor, R – is the gas constant, β is the linear heating

Table 2 Kinetic model investigated

Symbol	$g(\alpha)$	Macromechanism
D1	α	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 eq.
D4	$3/2[1-2\alpha/3-(1-\alpha)^{2/3}]$	three dimensional diffusion; spherical symmetry, Ginstling Brounshtein eq.
F1	$[-\ln(1-\alpha)]$	random nucleation; only one nucleus on each particle
A2	$[-\ln(1-\alpha)]^{1/2}$	random nucleation; Avrami I eq.
A3	$[-\ln(1-\alpha)]^{1/3}$	random nucleation; Avrami II eq.
R1	α	phase boundary reaction (zero order); Polanyi-Wigner eq.
R2	$2[1-(1-\alpha)^{1/2}]$	phase boundary reaction; cylindrical symmetry
R3	$3[1-(1-\alpha)^{1/3}]$	phase boundary reaction; spherical symmetry

rate, E – is the apparent activation energy. The thermodynamic parameters were calculated from the Eyring equation:

$$k(T) = \frac{k_B T}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) \quad (2)$$

where k_B – is the Boltzman constant, h – is the Planck constant, ΔS^* – is the entropy of activation, ΔH^* – is the enthalpy of activation.

Based on the $\alpha(T)$ dependences (Fig. 2), the $g(\alpha)$ function was chosen from among the well-known models (Table 2), which best described the experimental results of the decomposition. Values of the apparent activation energy, preexponential factor, linear regression coefficient r , entropy, enthalpy and free energy of activation obtained from an analysis of the dynamic TG curves on the basis of the Coats-

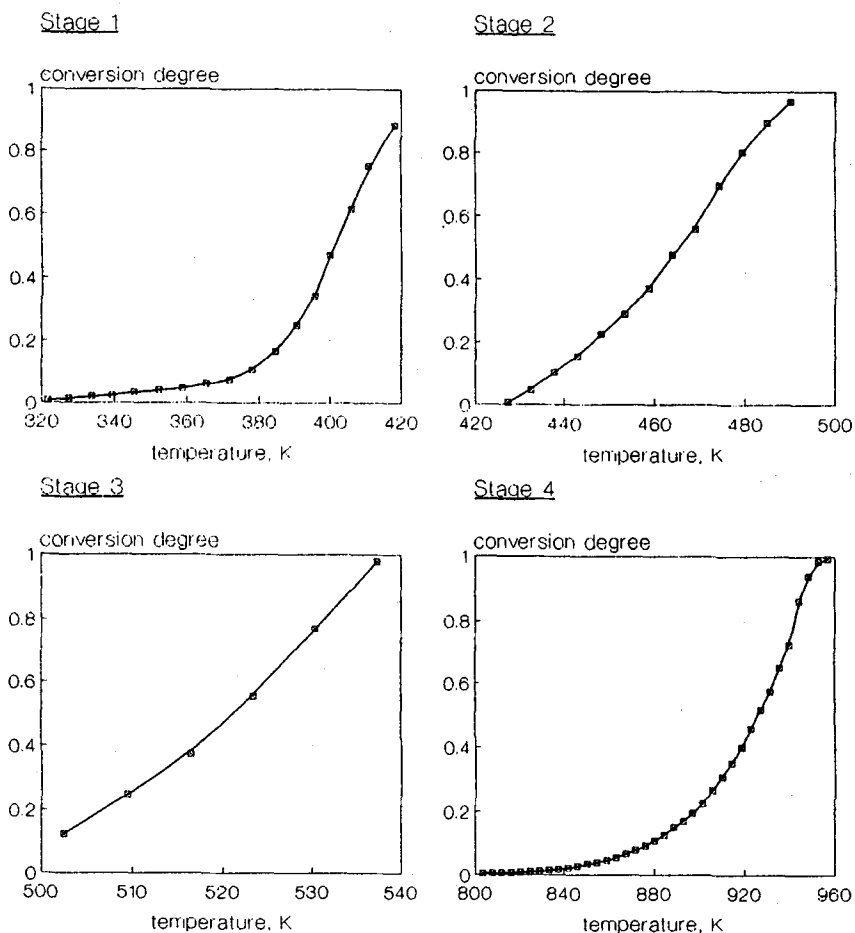


Fig. 2 Variation of conversion degree with temperature for different stages of decomposition of $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$

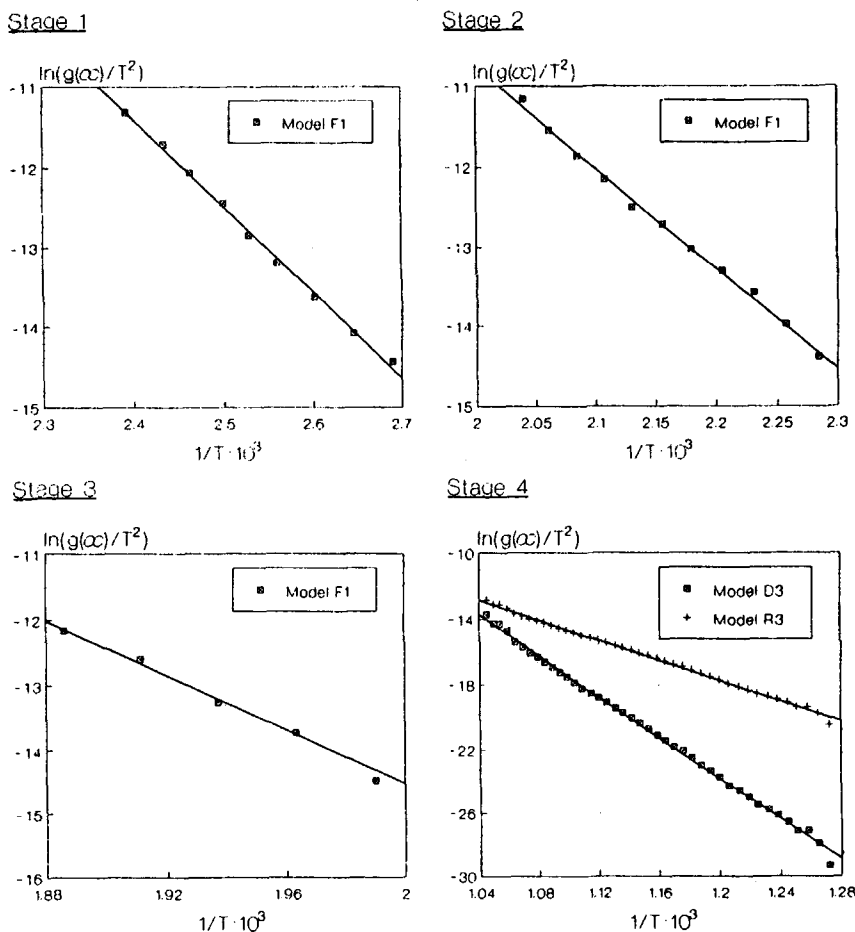


Fig. 3 Dependences of $\ln(g(\alpha)/T^2)$ on $1/T$ for the best models of decomposition of $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$

Redfern equation, are listed in Table 3. The course of the function $\ln(g(\alpha)/T^2)$ vs. $1/T$ for the best fitting models are shown in Fig. 3. From Table 3 it can be seen that the best fitting expression for all dehydration stages is the model F1. The activation energies increased from 89.82 for the first stage through 105.04 kJ mol^{-1} for the second stage to 172.62 kJ mol^{-1} for the last dehydration step. The last water semi-molecule was more strongly bound. The decomposition of anhydrous iron sulphate is controlled by the three dimensional diffusion model D3 or the contracting volume model R3. In this case it is impossible to choose one kinetic model from dynamic measurements.

The dependences of reaction rates on temperature for particular stages of decomposition which were calculated from the obtained kinetics equations are presented in Fig. 4. It seems that some stages of dissociation are partly overlapping.

Table 3 Kinetic and statistical parameters values from dynamic TG experiments

Stage	Model	E/ kJ mol ⁻¹	A/ min ⁻¹	ΔS^{\ddagger} / J (mol K) ⁻¹	ΔH^{\ddagger} / kJ mol ⁻¹	ΔG^{\ddagger} / kJ mol ⁻¹	Statistical parameters		
							r	s	F
1	D1	141.54	3.18·10 ¹⁷	45.0	138.1	190.4	0.9931	0.212	505
	D2	154.06	9.40·10 ¹⁸	73.2	150.6	120.2	0.9963	0.170	937
	D3	169.58	4.80·10 ²⁰	105.9	166.1	122.2	0.9984	0.121	2217
	D4	159.18	1.65·10 ¹⁹	77.9	155.7	123.4	0.9973	0.150	1271
	F1	89.82	1.34·10 ¹¹	-77.0	86.4	118.3	0.9985	0.063	2303
	A2	41.64	4.48·10 ⁴	-201.2	38.2	121.4	0.9983	0.031	2030
	A3	25.57	2.73·10 ²	-243.4	22.1	123.1	0.9980	0.020	1767
	R1	67.50	8.42·10 ⁷	-138.3	64.0	121.4	0.9924	0.107	454
	R2	77.69	2.47·10 ⁹	-110.2	74.2	120.0	0.9975	0.070	1378
R3	81.51	8.71·10 ⁹	-99.7	78.1	119.5	0.9983	0.061	2040	
2	D1	143.87	1.21·10 ¹⁵	-2.4	139.9	141.1	0.9838	0.269	271
	D2	162.64	1.13·10 ¹⁷	35.3	158.7	141.8	0.9918	0.215	543
	D3	188.59	4.95·10 ¹⁹	85.8	184.6	143.6	0.9979	0.124	2181
	D4	171.06	3.90·10 ¹⁷	45.6	167.1	145.3	0.9946	0.183	823
	F1	105.04	1.44·10 ¹¹	-77.6	101.1	138.1	0.9984	0.060	2878
	A2	48.67	4.13·10 ⁴	-202.8	44.7	141.6	0.9982	0.030	2499
	A3	29.88	2.38·10 ²	-245.7	25.9	143.4	0.9979	0.020	2142
	R1	68.09	4.33·10 ⁶	-164.1	64.1	142.6	0.9818	0.135	240
	R2	84.06	4.01·10 ⁸	-126.5	80.1	140.5	0.9954	0.083	967
R3	90.45	2.43·10 ⁹	-111.5	86.5	139.8	0.9977	0.063	1975	

Table 3 Continued

Stage	Model	E/ kJ mol ⁻¹	A/ min ⁻¹	ΔS^* / J (mol K) ⁻¹	ΔH^* / kJ mol ⁻¹	ΔG^* / kJ mol ⁻¹	tical parameters		
							r	F	
3	D1	242.79	4.06·10 ²³	159.8	238.3	152.5	0.9930	0.141	142
	D2	274.26	4.12·10 ²⁶	217.4	269.8	153.1	0.9951	0.134	202
	D3	312.86	1.51·10 ³⁰	285.6	308.4	155.0	0.9967	0.126	298
	D4	287.02	2.98·10 ²⁷	233.8	282.6	157.0	0.9957	0.130	234
	F1	172.62	8.17·10 ¹⁶	31.6	168.2	151.2	0.9971	0.064	348
	A2	81.99	3.99·10 ⁷	-146.6	77.5	156.3	0.9968	0.032	314
	A3	51.78	2.68·10 ⁴	-207.4	47.3	158.7	0.9965	0.021	282
	R1	117.08	1.04·10 ¹¹	-81.2	112.6	156.2	0.9925	0.071	131
	R2	142.62	5.47·10 ¹³	-29.2	138.2	153.8	0.9958	0.064	237
4	R3	152.11	5.56·10 ¹⁴	-9.9	147.6	153.0	0.9965	0.063	281
	D1	488.46	2.81·10 ²⁶	209.5	480.6	282.2	0.9967	0.328	5896
	D2	504.80	1.56·10 ²⁷	223.7	496.9	285.1	0.9982	0.248	11049
	D3	526.52	1.26·10 ²⁸	241.1	518.6	290.4	0.9988	0.213	16253
	D4	511.82	1.46·10 ²⁷	223.1	504.2	292.6	0.9986	0.221	14272
	F1	268.34	1.91·10 ¹⁴	-23.5	260.5	282.7	0.9969	0.175	6258
	A2	126.96	1.14·10 ⁰⁶	-180.9	119.1	290.4	0.9966	0.087	5675
	A3	79.84	1.77·10 ⁰³	-234.7	72.0	294.2	0.9962	0.058	5111
	R1	237.02	1.82·10 ¹²	-62.2	229.1	288.0	0.9964	0.165	5463
R2	250.67	1.39·10 ¹³	-45.3	242.8	285.7	0.9987	0.107	14593	
R3	256.05	3.00·10 ¹³	-38.6	248.2	284.8	0.9987	0.107	15293	

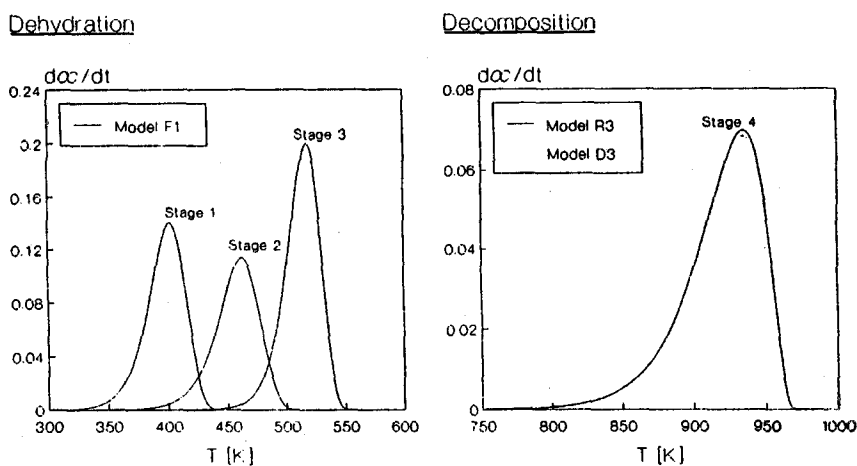


Fig. 4 Variation of reaction rates with temperature for different stages of decomposition of $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$

Conclusions

The thermal decomposition of iron(III) sulphate hexahydrate occurs in four steps under the conditions applied in this study. The elimination of water occurs in three steps with the corresponding endothermic peaks at 415, 478, 537 K. All stages of dehydration are governed by nucleation model F1. The activation energy of the dehydration processes increases with decreasing hydration number of the iron from 89.82 to 172.62 kJ mol^{-1} .

The decomposition of anhydrous iron sulphate occurs in the temperature range between 810 and 960 K. The kinetics of this process is controlled by the three-dimensional diffusion model D3 or the contracting volume model R3. The activation energies are 526.52 or 256.05 kJ mol^{-1} , respectively.

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References

- 1 P. G. Coombs and Z. M. Muniev, *J. Thermal Anal.*, 35 (1989) 967.
- 2 V. V. Pechkovski, A. G. Zvezdon and S. V. Ostrovski, *J. Appl. Chem. USSR*, 36 (1963) 1403.
- 3 T. P. Prasad, *J. Inorg. Nucl. Chem.*, 34 (1972) 1994.
- 4 V. Balek, K. Habersberger, *Thermal Anal.*, Vol. 2, Proc. 3rd ICTA Davos 1971, p. 501.
- 5 J. Straszko, M. Olszak-Humienik and J. Możejko, *Inż. Chem. i Proc.*, 1 (1995) 45.