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STUDY OF THE MECHANISM AND KINETIC PARAMETERS OF THE THERMAL DECOMPOSITION OF COBALT SULPHATE HEXAHYDRATE

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Abstract

Thermogravimetry (TG-DTG), and differential thermal analysis (DTA) were used in the study of the kinetics of decomposition of cobalt sulphate hexahydrate under an air atmosphere.

The kinetics of the particular stages of $CoSO_4{\cdot}6H_2O$ decomposition were evaluated from the dynamic mass loss data. The values of the kinetic parameters for each stage of the thermal decomposition were calculated from the $\alpha(T)$ data by using the integral method, applying the Coats-Redfern approximation.

Keywords: $CoSO_4{\cdot}6H_2O$, kinetics, thermal decomposition

Introduction

The thermal decomposition of cobalt sulphate and the kinetics of the process have been studied as part of a programme involving investigation of the thermal dissociation of transition element sulphates.

A number of papers have reported on the many stages of pyrolysis of cobalt sulphate hydrates [1–4], but the mechanisms and the kinetic parameters of these reactions have not been described unequivocally. The following reactions occur in the course of the thermal decomposition of $CoSO_4{\cdot}6H_2O$ [1]:

$$CoSO_4{\cdot}6H_2O \rightarrow CoSO_4{\cdot}4H_2O+2H_2O$$

$$CoSO_4{\cdot}4H_2O \rightarrow CoSO_4{\cdot}H_2O+3H_2O$$

$$CoSO_4{\cdot}H_2O \rightarrow CoSO_4+H_2O$$

$$CoSO_4 \rightarrow CoO+SO_3$$

The energy of activation has been reported only for the stage of decomposition of anhydrous cobalt sulphate to cobalt oxide: 318–319 kJ mol^{-1} for the decomposition

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in air [5, 6] and 222 kJ mol^{-1} in oxygen and nitrogen [5]. In both cases, the reaction was described by contracting volume model R3.

The aim of the present work was to study the mechanism [7] of thermochemical decomposition of hydrated cobalt sulphate and to calculate the kinetic and thermodynamic parameters.

The kinetics of thermal decomposition of $CoSO_4 \cdot 6H_2O$ was followed by the integral method by applying the Coats-Redferns approximation:

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

where α – transformation degree, $g(\alpha)$ – conversion function dependent on the mechanism of the reaction, T– absolute temperature/K, R – gas constant/J mol^{-1} K^{-1}, q – linear heating rate/K min^{-1}, E – apparent activation energy/kJ mol^{-1} and A – pre-exponential Arrhenius factor min^{-1}.

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 for the correct model relation. A comparison with other methods of assessing the kinetic parameters has been presented previously [7].

The thermodynamic parameters of activation can be calculated via the equations

$$\Delta H^{*}=E-RT \qquad (2)$$

$$\Delta S^{*}=R\left(\ln\frac{hA}{k_{\mathrm{B}}T}-1\right) \qquad (3)$$

$$\Delta G^{*}=\Delta H^{*}-T\Delta S^{*} \qquad (4)$$

where ΔH^* – enthalpy of activation/kJ mol^{-1}, ΔS^* – entropy of activation/J mol^{-1} K^{-1}, ΔG^*– free enthalpy of activation kJ mol^{-1} , h – Planck constant and k_{B} – Boltzmann constant.

The following parameters were calculated to aid the selection of the $g(\alpha)$ function best describing the experimental results: the correlation coefficient r, the standard error of estimation s, and Snedecor's variable F. Additionally, to eliminate other models, the results were analysed by using a series test.

Experimental

The initial crystalline salt $CoSO_4 \cdot 6H_2O$ used in the present investigation of analytical grade, was supplied by P. P. H. Polskie Odczynniki Chemiczne, Gliwice, Poland.

Measurements were carried out on a Hungarian MOM 1500 derivatograph. The operational characteristics were as follows: heating rate: 5 deg min^{-1}; sample size: 300 and 700 mg; atmosphere: static air and temperature range: 20–1000°C.

Results

The TG, DTG and DTA curves of the investigated compound are shown in Fig. 1. The characteristic temperatures of decomposition and the mass losses of the samples for particular stages are presented in Table 1.

Table 1 Thermal analysis data on $CoSO_4\cdot 6H_2O$

Stage	Temperature range/K	DTA peak temperature/K	Mass loss/%	
			found	theoretical
1	320–391	384	12.64	13.68
2	391–515	403	19.71	20.52
3	540–628	598	6.89	6.84
4	1000–1235	1189	31.00	30.45

The decomposition started at about 320 K. The following reactions were observed under the conditions of the experiment: partial dehydration to the tetrahydrate and monohydrate, formation of anhydrous sulphate, and formation of CoO. Formed at around 628 K, anhydrous cobalt sulphate is stable up to 1000 K. The decrease in mass ceased at about 1235 K. The data obtained agree with those in a previous publication [1].

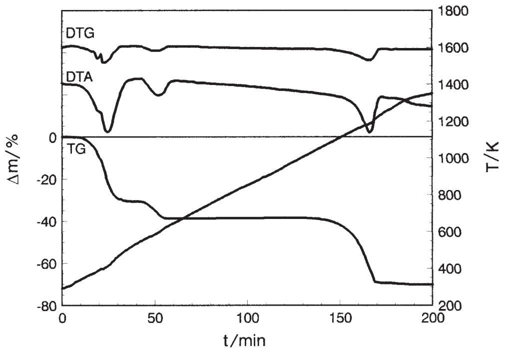

Fig. 1 Thermal decomposition curves for a 700 mg sample of $CoSO_4\cdot 6H_2O$

All decomposition reactions were associated with endopeaks. The effects associated with dehydration were not clearly outlined in the curves. The DTA curve displayed a double peak relating to the intermediate (mesophase) in the dehydration of the hexahydrate.

The TG curve data were used to derive the mechanism of the individual stages, and their activation energies and pre-exponential factors were calculated. From the observed mass losses, the α *vs.* T relations for the particular steps were estimated, and from the $\alpha(T)$ curves (Fig. 2), the $g(\alpha)$ functions from the well-known models [7] were chosen. The values of the kinetic, thermodynamic and statistical parameters for

Table 2 Kinetic and statistical parameter values from dynamic TG experiments

Stage	Model	E/ kJ mol^{-1}	A/ min^{-1}	Statistical parameter			ΔS^*/ J mol^{-1} K^{-1}	ΔH^*/	ΔG^*/
				r	s	F		kJ mol^{-1}	
1	D1	150	$1.29\cdot10^{20}$	0.9956	0.311	1348	96	147	110
	D2	154	$2.92\cdot10^{20}$	0.9967	0.278	1789	102	151	112
	D3	159	$5.19\cdot10^{20}$	0.9975	0.248	2381	107	156	114
	D4	156	$1.70\cdot10^{20}$	0.9970	0.266	1983	98	153	115
	F1	79	$2.27\cdot10^{10}$	0.9977	0.117	2641	–91	76	111
	A2	36	$1.88\cdot10^{04}$	0.9973	0.056	2245	–208	33	113
	A3	22	$1.56\cdot10^{02}$	0.9968	0.039	1882	–247	19	114
	R1	72	$1.88\cdot10^{09}$	0.9951	0.157	1227	–112	69	112
	R2	75	$6.22\cdot10^{09}$	0.9969	0.131	1912	–102	72	111
	R3	76	$9.47\cdot10^{09}$	0.9973	0.125	2187	–98	73	111
2	D1	97	$1.20\cdot10^{11}$	0.8971	0.529	33	–78	94	125
	D2	116	$2.12\cdot10^{13}$	0.9241	0.531	47	–35	113	126
	D3	144	$4.55\cdot10^{16}$	0.9553	0.495	84	29	141	129
	D4	123	$1.19\cdot10^{14}$	0.9360	0.521	57	–20	122	130
	F1	85	$1.22\cdot10^{10}$	0.9741	0.219	149	–97	82	121
	A2	39	$1.17\cdot10^{04}$	0.9692	0.110	124	–212	36	121
	A3	24	$1.01\cdot10^{02}$	0.9628	0.074	102	–251	20	122
	R1	45	$3.88\cdot10^{04}$	0.8828	0.265	28	–202	42	123
	R2	62	$7.70\cdot10^{06}$	0.9360	0.257	57	–158	58	122
	R3	67	$6.98\cdot10^{07}$	0.9508	0.248	75	–140	65	122

Table 2 Continued

Stage	Model	E/ kJ mol^{-1}	A/ min^{-1}	Statistical parameter			ΔS^*/ J mol^{-1} K^{-1}	ΔH^*/	ΔG^*/
				r	s	F		kJ mol^{-1}	
3	D1	184	$1.65\cdot10^{15}$	0.9609	0.338	108	–2	179	180
	D2	216	$9.88\cdot10^{17}$	0.9762	0.307	182	51	211	181
	D3	265	$1.16\cdot10^{22}$	0.9912	0.255	505	129	260	183
	D4	232	$9.55\cdot10^{18}$	0.9823	0.282	248	70	227	185
	F1	156	$1.60\cdot10^{13}$	0.9977	0.067	1949	–40	151	175
	A2	73	$4.12\cdot10^{05}$	0.9973	0.034	1684	–186	68	179
	A3	45	$1.05\cdot10^{03}$	0.9969	0.023	1441	–235	40	181
	R1	87	$4.49\cdot10^{06}$	0.9565	0.169	97	–166	82	181
	R2	116	$2.51\cdot10^{09}$	0.9841	0.133	277	–113	111	178
	R3	127	$3.46\cdot10^{10}$	0.9905	0.113	465	–91	123	177
4	D1	592	$2.14\cdot10^{25}$	0.9974	0.232	6962	186	582	360
	D2	617	$2.04\cdot10^{26}$	0.9981	0.218	9426	205	607	364
	D3	650	$2.98\cdot10^{27}$	0.9985	0.188	11856	227	641	370
	D4	628	$2.33\cdot10^{26}$	0.9983	0.192	10925	206	618	373
	F1	334	$1.19\cdot10^{14}$	0.9956	0.170	4027	–29	325	359
	A2	158	$8.57\cdot10^{05}$	0.9951	0.084	3626	–185	148	368
	A3	99	$1.42\cdot10^{03}$	0.9945	0.056	3240	–238	89	373
	R1	287	$4.73\cdot10^{11}$	0.9972	0.117	6422	–75	277	366
	R2	308	$5.54\cdot10^{12}$	0.9980	0.109	8907	–55	298	363
	R3	316	$1.43\cdot10^{13}$	0.9984	0.096	11044	–47	306	362

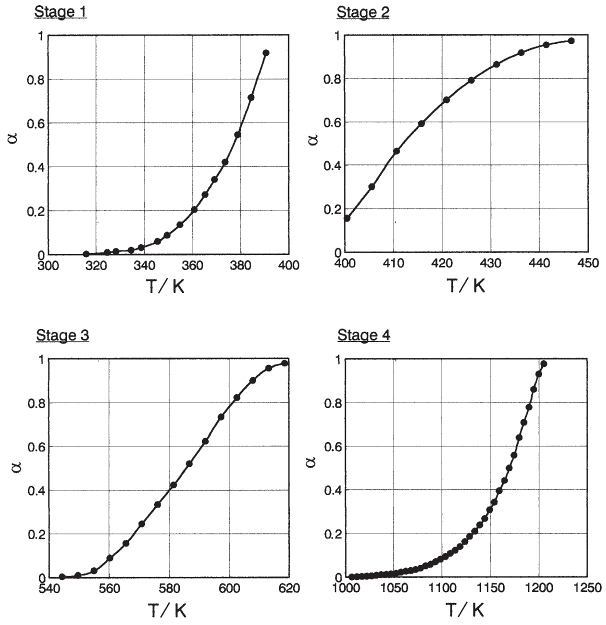

Fig. 2 The function $\alpha(T)$ for the thermal decomposition of $CoSO_4 \cdot 6H_2O$

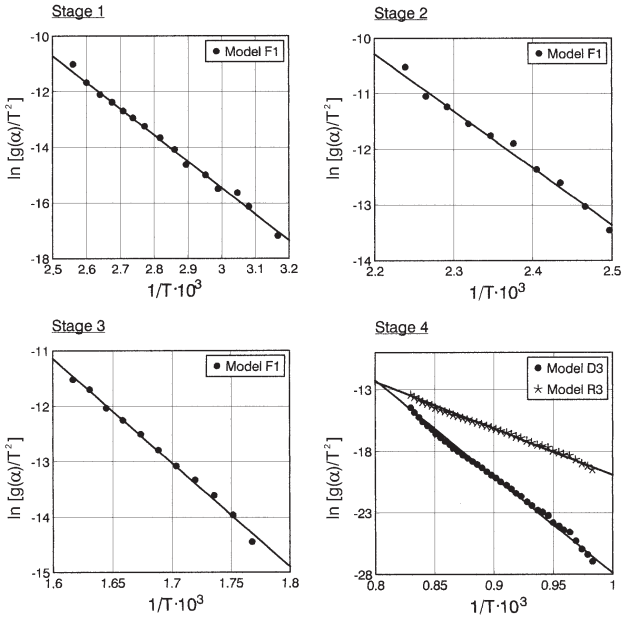

Fig. 3 Arrhenius plots for the thermal decomposition of $CoSO_4 \cdot 6H_2O$

all analysed models are listed in Table 2. The Arrhenius plots for the best-fitting model for the particular steps are depicted in Fig. 3. The parameters chosen on the basis of the series test for the best models are listed in Table 3.

Table 3 Kinetic parameters for the best models

Stage	Model	*E*/ kJ mol^{-1}	*A*/ min^{-1}	Δ*S**/ J mol^{-1} K^{-1}	Δ*H**/ kJ mol^{-1}	Δ*G**/ kJ mol^{-1}
1	F1	79	$2.27\cdot10^{10}$	–91	76	111
2	F1	85	$1.22\cdot10^{10}$	–97	82	121
3	F1	156	$1.60\cdot10^{13}$	–40	151	175
4	D3	650	$2.98\cdot10^{27}$	227	641	370
	R3	316	$1.43\cdot10^{13}$	–47	306	362

From Table 3, it can be seen that the best-fitting expressions for the dehydration stages are those of the random nucleation model F1 with apparent activation energies of 79, 85 and 156 kJ mol^{-1}, respectively. The highest values of E for the last dehydration stage reflect the fact that the final water molecule is most strongly bound.

The desulphurization reaction to cobalt oxide is controlled by three-dimensional diffusion model D3 or contracting volume model R3. The experimental results for this stage of decomposition confirm the problem that in some cases it is impossible to choose one kinetic model from dynamic measurements.

The dependences of the reaction rates on temperature in the particular stages of decomposition are presented in Fig. 4. This figure reveals that the highest rate is observed for the first stage of decomposition.

Figure 5 compares the values of the thermodynamic functions of the reactants from [8] without thermodynamic function values for the active complex, obtained on the basis of the experimental results for the final decomposition step from Eq. (4).

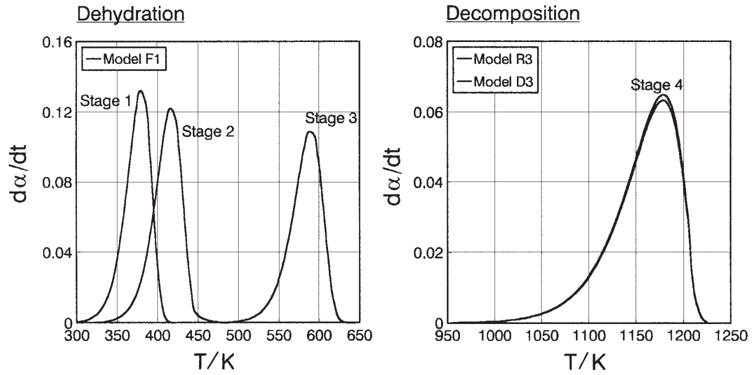

Fig. 4 Variation of reaction rate with temperature for the decomposition of $CoSO_4 \cdot 6H_2O$

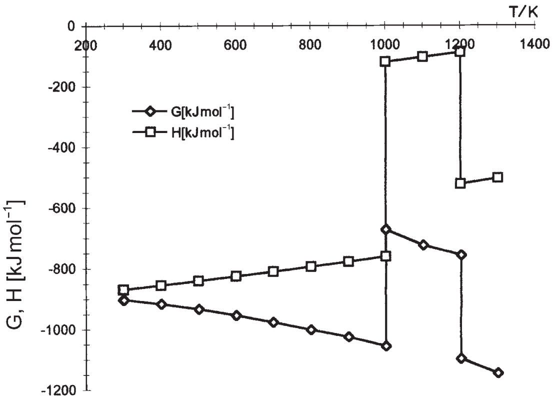

Fig. 5 Comparison of the thermodynamic function of the reactant with the thermodynamic function of activation for the reaction of desulphuration of $CoSO_4$

Conclusions

The results clearly show that the thermal decomposition of cobalt sulphate hexahydrate occurs in four steps. The elimination of water takes place in the first three stages of decomposition. These reactions are regulated by random nucleation model F1 with activation energies increasing from 79 to 156 kJ mol^{-1} and pre-exponential factors of $1.22{\cdot}10^{10}$–$1.60{\cdot}10^{13}$ min^{-1}.

The desulphurization step is governed by the three-dimensional diffusion model D3 or the contracting volume model R3, with an apparent activation energy of 650 or 316 kJ mol^{-1}, respectively.

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