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Thermodynamic functions of activated complexes created in thermal decomposition processes of sulphates

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Abstract

The thermal decomposition of transition metal sulphates was studied by thermogravimetry in static air. The TG, DTG and DTA curves were obtained using a Hungarian MOM C-derivatograph. Kinetic analysis of experimental TG-curves was carried out by applying the Coats and Redfern's equation. The thermodynamic functions of transient states were calculated from the Eyring equation. The thermal decomposition of investigated sulphates can be described by kinetic equation $d\alpha/dt = A \cdot \exp(-(E/RT)) \cdot (1-\alpha)^n$. The reaction order for all investigated sulphates is at short range 2/3. The thermal stability of sulphates increased with radius of the cation. The dependence of free enthalpy of activation complexes on decomposition temperature and radius of cation is rectilinear. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Transient metal sulphates; Thermal decomposition; Kinetics of the thermal decomposition; Thermodynamic function of activation complexes

1. Introduction

The salts of transition metals are widely scattered in nature, they have great technical importance and have been extensively studied by means of thermal analysis methods [1–6]. The data concerning the thermal behaviour of transition metal sulphates have not been systematised yet.

The sulphates decompose on heating releasing SO_3 or SO_2 and giving a residue in the form of oxides. The oxides may exhibit the thermal stability or may undergo a number of transformations with an increase of temperatures.

The investigated sulphates with atomic numbers ranging from 24 to 30 are divided into two completely different classes. The first class includes sulphates with atomic numbers ranging from 24 to 28 with unfilled d-orbital, which decompose in one step. The second class includes sulphates with atomic numbers 29 and 30, respectively, which decompose on heating giving the intermediate products — basic salts.

Our previous works [3–6] were undertaken to analyse the different kinetic models of decomposition and were referred to the investigations of the samples with larger mass.

This paper will review the types of sulphates of transition metals that have been tested, the factors that limit their activity, and the kinetics and mechanism of the decomposition reactions.

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The kinetics of thermal dissociation can be adequately described by a simple equation

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot (1-\alpha)^n, \tag{1}$$

where α is the transformation degree, n the order of the reaction, T the temperature in K, R the gas constant in J mol^{-1} K^{-1}, t the time in min, E the apparent activation energy in kJ mol^{-1}, and A is the pre-exponential Arrhenius factor in min^{-1}.

The kinetics of thermal decomposition of investigated sulphates was followed by the integral method by applying the Coats–Redferns approximation:

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

where q is the linear heating rate in K min^{-1}.

The equation is frequently used to describe the kinetics of thermal decomposition of the solids in general. A plot of $\ln[(1-(1-\alpha)^{(1-n)})/(T^2(1-n))]$ vs. $1/T$ gives a straight line for the correct model reaction.

The thermodynamic parameters of activation can be calculated from the equations:

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

$$\Delta H^* = E - RT, \tag{4}$$

$$\Delta S^* = R\left(\ln\frac{hA}{k_B T} - 1\right), \tag{5}$$

$$\Delta G^* = \Delta H^* - T\Delta S^*, \tag{6}$$

where ΔH^* is the enthalpy of activation in kJ mol^{-1}, ΔS^* the entropy of activation in J mol^{-1} K^{-1}, ΔG^* the free energy of activation in kJ mol^{-1}, h the Planck constant, and k_B is the Boltzmann constant.

2. Experimental

The initial salts, analytical grade, used in the present investigations were supplied by P.P.H. Polskie Odczynniki Chemiczne, Gliwice, Poland. The salts were initially dried at 250°C.

The thermogravimetric measurements were carried out on the Hungarian derivatograph MOM C. The operational characteristics are as follows:

- heating rate: 5 K min^{-1};
- sample size: 50 mg;
- atmosphere: static air;
- temperature range: 20–1000°C.

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

3. Results

On the basis of our study we can state that the following reactions take place during the thermal decomposition of studied sulphates (Table 1).

From the mass losses in the TG-curves the α–T relations for the particular salts were estimated (Fig. 1). Based on the $\alpha(T)$ dependence, the $(1-\alpha)^n$ function which described best the experimental results of the decomposition were chosen. The

Table 1
Decomposition reactions

Number	Reaction	T_{range} (K)	$T_{\text{DTG peak}}$ (K)
1	$Cr_2(SO_4)_3 \rightarrow Cr_2O_3 + 3SO_3$	838–1007	979
2	$MnSO_4 \rightarrow MnO + SO_3$	1023–1243	1218
3	$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$	839–1005	980
4	$2CoSO_4 \rightarrow Co_2O_3 + SO_3 + SO_2$	1020–1176	1150
5	$NiSO_4 \rightarrow NiO + SO_3$	972–1135	1111
6a	$2CuSO_4 \rightarrow CuO{\cdot}CuSO_4 + SO_3$	930–1033	1016
6b	$CuO{\cdot}CuSO_4 \rightarrow 2CuO + SO_3$	1033–1104	1086
7a	$3ZnSO_4 \rightarrow ZnO{\cdot}2ZnSO_4 + SO_3$	936–1099	1077
7b	$ZnO{\cdot}2ZnSO_4 \rightarrow 3ZnO + 2SO_3$	1099–1239	1221

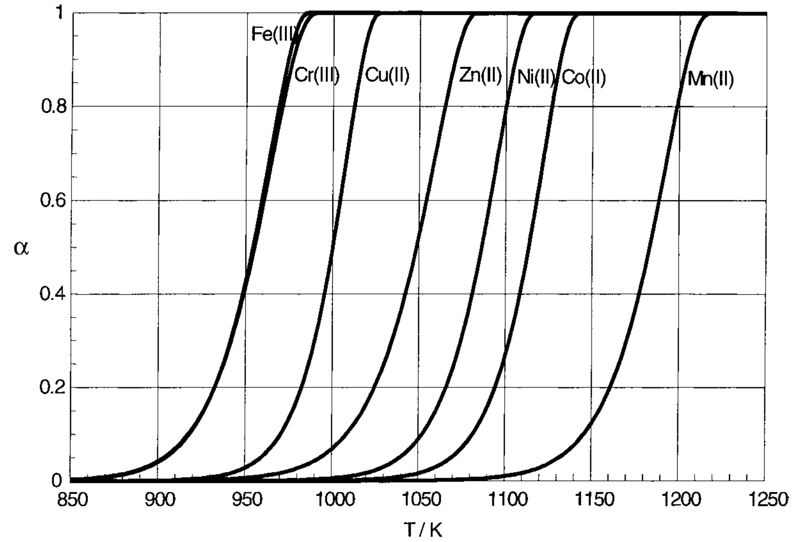

Fig. 1. Dependence of transformation degrees on temperature.

values of the entropy, enthalpy and free energy of activation obtained on the basis of Eqs. (3)–(6) are listed in Table 2.

Fig. 2 shows the changes of decomposition temperatures of sulphates with atomic numbers of cations. The lowest decomposition temperatures of decomposition are for the sulphates of trivalent elements; manganese sulphate had the highest decomposition temperature.

Fig. 3 shows the values of free enthalpy of activated complexes, which decides the thermal stability calculated from Eyring Eq. (3), and entropy with decomposition temperature for various salts. The changes of activation enthalpy and entropy with the decomposition temperature in Fig. 4 shows a similar character.

From Fig. 5 it can be seen that the dependence of free enthalpy of activation on the decomposition temperature of particular sulphates is rectilinear.

Fig. 6 presents the dependence of ΔG^{*} function vs. the radius of the cation [7], which is also rectilinear. The effect of decomposition temperature on the radius of the cation in Fig. 7 is similar.

Table 2
Thermodynamic functions of activated complexes

Cation	Electron configuration	Radius of the cation (Å)	$T_{\mathrm{DTG\ peak}}$ (K)	Kinetic order	ΔS^{*} (J mol^{-1} K^{-1})	ΔH^{*} (kJ mol^{-1})	ΔG^{*} (kJ mol^{-1})
Cr(III)	[Ar]3d^{5}4s^1	0.67	1007	0.69	34	324	291
Mn(II)	[Ar]3d^{5}4s^2	0.69	1243	0.68	121	509	361
Fe(III)	[Ar]3d^{6}4s^2	0.69	1005	0.66	45	333	290
Co(II)	[Ar]3d^{7}4s^2	0.72	1176	0.67	172	530	333
Ni(II)	[Ar]3d^{8}4s^2	0.74	1135	0.66	129	472	328
Cu(II)	[Ar]3d^{10}4s^1	0.74	1033	0.67	158	461	301
Zn(II)	[Ar]3d^{10}4s^2	0.80	1099	0.61	39	363	320

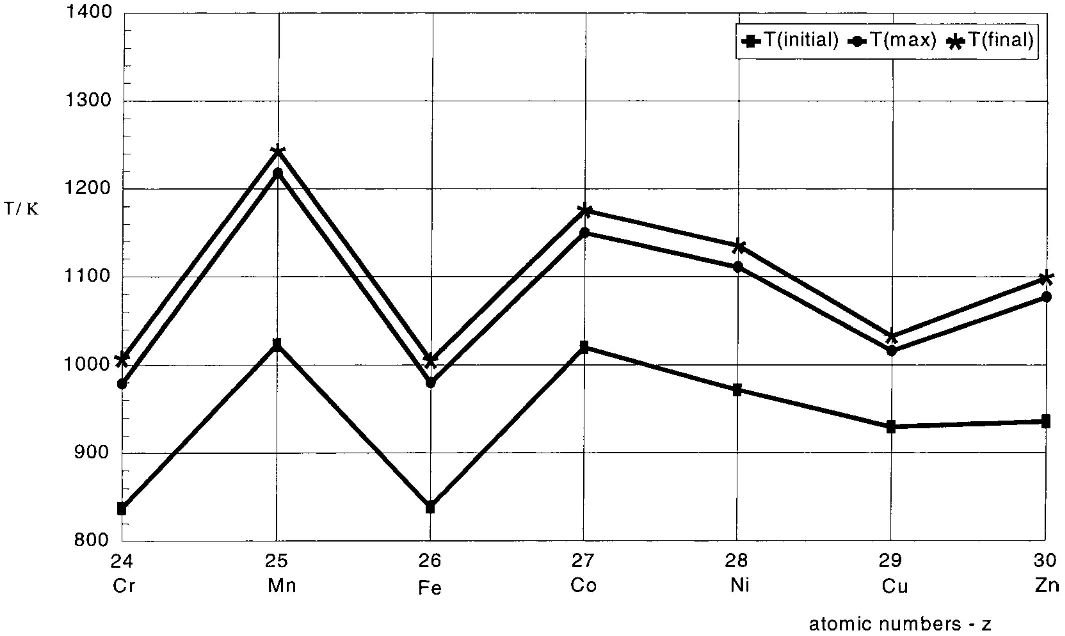

Fig. 2. The decomposition temperatures of various sulphates.

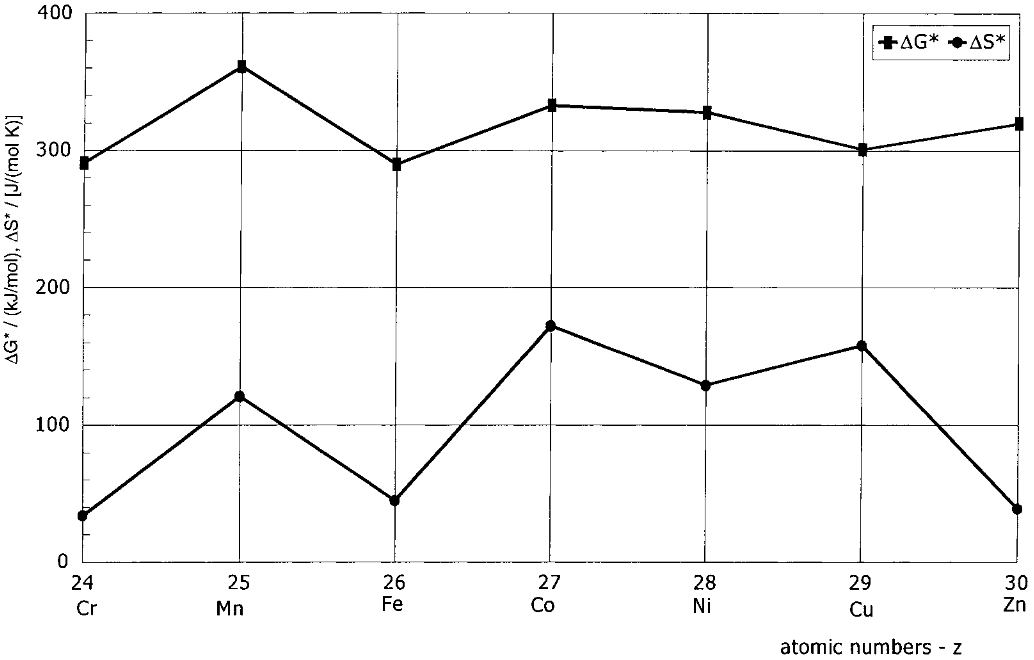

Fig. 3. Thermodynamic functions of activated complexes created in thermal decomposition of various sulphates.

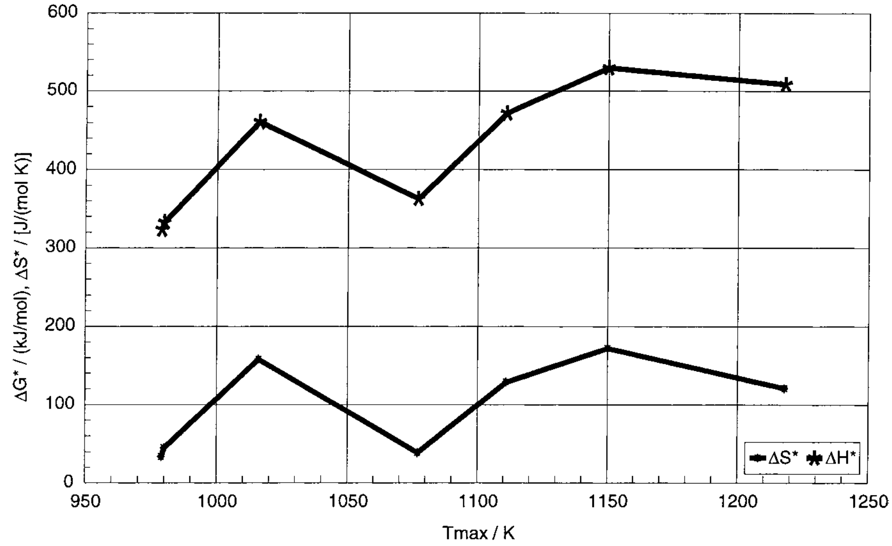

Fig. 4. Dependence of the ΔH^* and ΔS^* functions on decomposition temperatures.

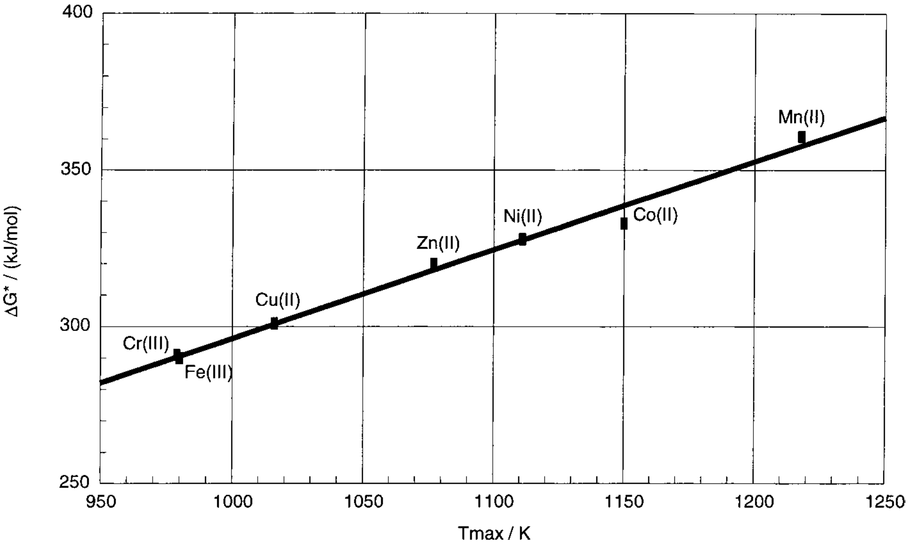

Fig. 5. Dependence between the ΔG^* function and the decomposition temperature of various sulphates.

4. Conclusions

The thermal decomposition of investigated sulphates can be described by kinetic equation $d\alpha/dt = A \cdot \exp(-(E/RT)) \cdot (1-\alpha)^n$.

The results presented above show that the reaction order for all investigated sulphates is at short range 2/3. The value is close to the kinetic model R3.

The thermal stability of sulphates increased with the radius of the cation. The lowest temperatures of

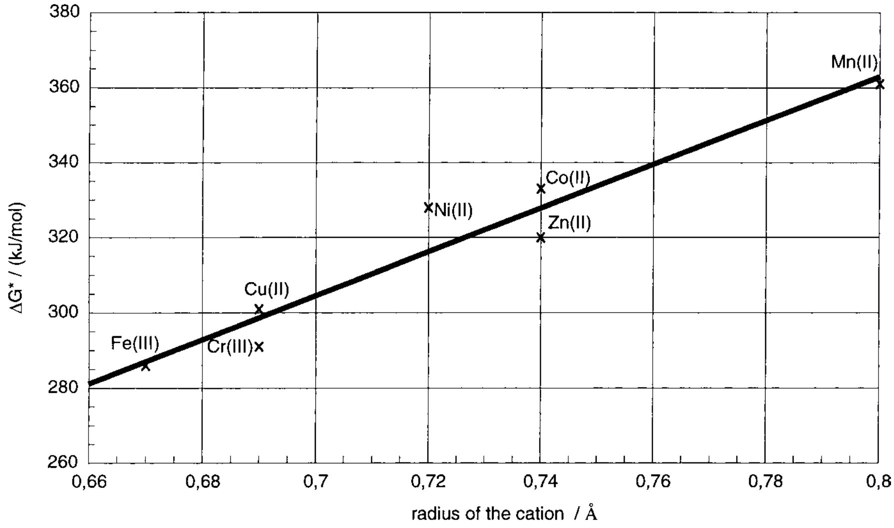

Fig. 6. Variation of values of the ΔG^* function with radius of the cation of sulphates.

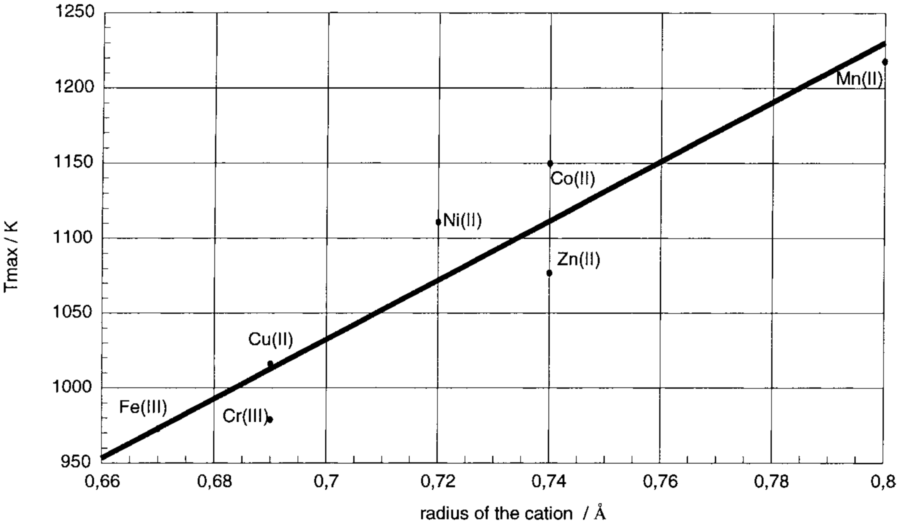

Fig. 7. Variation of decomposition temperatures of sulphates with radius of the cation.

decomposition are for the sulphates of trivalent elements; manganese sulphate had the highest decomposition temperature.

The dependence of free enthalpy of activation complexes on decomposition temperature and radius of cation is rectilinear.

Acknowledgements

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