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THERMAL ANALYSIS OF IRON(II) SULPHATE HEPTAHYDRATE IN AIR. V

THERMAL DECOMPOSITION OF HYDROXY AND OXYSULPHATES

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The thermal decomposition of the hydroxysulphate and oxysulphate of iron(III) was carried out in air. Under dynamic conditions, the hydroxysulphate decomposes to the oxysulphate, which in turn decomposes to iron(III) oxide and sulphur oxides. The oxysulphate decomposes directly to iron(III) oxide and sulphur oxides. The heats of decomposition and heats of formation of the two basic sulphates were calculated.

The hydrosulphate, $Fe(OH)SO_4$, and oxysulphate, $Fe_2O(SO_4)_2$, of iron(III) are known to be formed during the thermal decomposition of iron(II) sulphate heptahydrate [1–11] and other hydrates of iron(II) sulphate [12–14]. Their study has therefore generally beeen confined to their occurrence as intermediates during the thermal decomposition of the hydrates of iron(II) sulphate. No attempts have been made to isolate these compounds and study their thermal decomposition behaviour. In our previous communications [12–14] we have given an account of these basic sulphates with respect to their formation during the thermal decomposition of iron(II) sulphate hydrates, and their preparation in pure form. In this communication, we present our results on the thermal decomposition behaviour of the hydroxy and oxysulphates of iron(III).

Experimental

Materials: The hydroxysulphate, $Fe(OH)SO_4$, and the oxysulphate, $Fe_2O(SO_4)_2$, were prepared as described earlier [12].

Apparatus: As described earlier [13].

Methods: X-ray, thermal analysis and thermochemical data were obtained by using appropriate methods and procedures [13–15].

Results and discussion

X-ray analysis

The compounds $Fe(OH)SO_4$ and $Fe_2O(SO_4)_2$ were examined by the X-ray powder diffraction method and the data are given in Table 1. It may be seen from the Table that the X-ray data for the hydroxysulphate from the present work compare fairly well with those given for in the ASTM card index. The data for $Fe_2O(SO_4)_2$ are not available from the card index. The data given by Safiullin et al. for their new phase (presumably $Fe_2O(SO_4)_2$) do not agree well with our data except for one line with "*d*" value 4.356. Confirmation of the data for this compound is therefore awaited.

Thermal analysis

Thermal decomposition curves for $Fe(OH)SO_4$ are presented in Fig. 1. Thermal and weight loss data are given in Table 2. From the results it will be seen that the hydroxysulphate, which is stable up to 125°, decomposes to an intermediate compound. From the weight loss data, the decomposition in the temperature range 125–620° can be represented by the equation:

$$2\,Fe(OH)SO_4 = Fe_2O(SO_4)_2 + H_2O\,. \tag{1}$$

Table 1

X-ray data for the basic sulphates of iron

Basic sulphate	"*d*" value, Å	Literature values
		2 $Fe(OH)SO_4$*
$Fe(OH)SO_4$	4.74	5.1
	3.55	4.78
	3.26	3.57
	2.33	3.26
	2.04	
	1.99	3.21
	1.83	1.83
	1.63	1.63
	1.59	1.59
	1.56	
$Fe_2O(SO_4)_2$		Compound X**
		5.976
	4.98	4.356
	4.36	3.626
	3.57	2.982
	3.19	
	3.14	
	2.72	
	2.49	
	2.39	
	2.28	
	1.84	

* ASTM Card No. 21–428.
** N. Sh. Safiullin et al. [3].

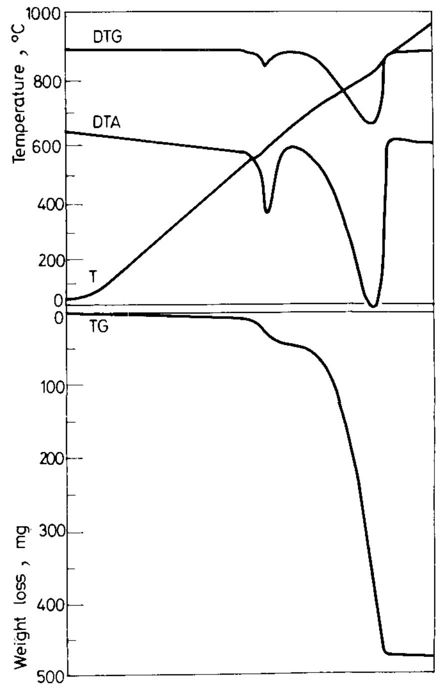

Fig. 1. TG, DTG and DTA curves of $Fe(OH)SO_4$

The intermediate decomposes further to iron(III) oxide and sulphur oxides, as represented by:

$$Fe_2O(SO_4)_2 = Fe_2O + 2\,SO_3\,. \tag{2}$$

From isothermal studies it has been shown [13, 14] that the hydroxysulphate decomposes to the oxysulphate, and that the oxysulphate in turn decomposes simultaneously to iron(III) sulphate and iron(III) oxide:

$$Fe_2O(SO_4)_2 \begin{cases} \nearrow Fe_2O_3 + SO_3 \\ \searrow Fe_2O_3 + Fe_2(SO_4)_2\,. \end{cases} \tag{3}$$

The iron(III) sulphate thus formed decomposes to iron(III) oxide and sulphur trioxide:

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3\,SO_3\,. \tag{4}$$

During dynamic thermal analysis, however, the oxysulphate decomposes directly to iron(III) oxide and sulphur oxides, as shown by the single-stage decomposition of the oxysulphate (cf. Fig. 1).

Table 2

Thermal and weight loss data for $Fe(OH)SO_4$

No.	Event	Temperature, °C	% Wt. loss Calcd.	% Wt. loss Obsd.
1. (a)	Stability of $Fe(OH)SO_4$	up to 125	—	—
(b)	Decomposition of $Fe(OH)SO_4$	125	5.30	5.00
(c)	DTG peak	580		
(d)	DTA peak	585		
(e)	Completion of decomposition	620		
2. (a)	Stability of the decomposition product, $Fe_2O(SO_4)_2$	*		
(b)	Decomposition to Fe_2O_3 $Fe_2O(SO_4)_2 = Fe_2O_3 + 2\,SO_3$**	660	50.00	50.30
(c)	DTG peak	815		
(d)	DTA peak	825		
(c)	Completion of decomposition	900		
3.	$2\,Fe(OH)SO_4 = Fe_2O_3 + 2\,SO_3 + H_2O$		52.70	52.80

* Not stable.
** Decomposes to SO_2 and O_2.

Thermal decomposition curves for the oxysulphate are presented in Fig. 2, and the thermal and weight loss data in Table 3. The weight loss corresponds to the following equation:

$$Fe_2O(SO_4)_2 = Fe_2O_3 + 2\,SO_3\,. \qquad (2)$$

The thermal decomposition curves reveal only a single process, indicating that the oxysulphate decomposes directly to iron(III) oxide and sulphur oxides.

Table 3

Thermal and weight loss data for $Fe_2O(SO_4)_2$

No.	Event	Temperature, °C	% Wt. loss Calcd.	% Wt. loss Obsd.
1. (a)	Stability of $Fe_2O(SO_4)_2$	up to 590		
(b)	Decomposition to Fe_2O_3 $Fe_2O(SO_4)_2 = Fe_2O_3 + 2\,SO_3$*	590	50.00	49.80
(c)	DTG peak	810		
(d)	DTA peak	815		
(e)	Completion of decomposition	880		

* Decomposes to SO_2 and O_2.

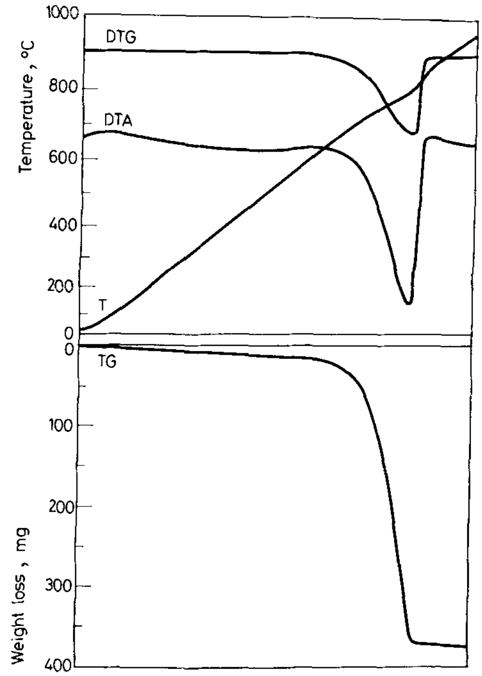

Fig. 2. TG, DTG and DTA curves of $Fe_2O(SO_4)_2$

Thermochemical parameters

The heats of decomposition and the heats of formation calculated from the heats of decomposition are given in Table 4. To calculate the heats of formation, it was assumed that the ΔH (heat of decomposition) obtained from the DTA curves holds approximately at 298 K. The heats of formation were calculated as follows:

$$2\,FeSO_4 \cdot 7\,H_2O + 1/2\,O_2 \overset{\Delta H}{=} Fe_2O(SO_4)_2 + 14\,H_2O\,. \qquad (5)$$

Table 4

Heats of decomposition and formation of basic sulphates of iron(III)

Decomposition reaction	Heat of decompn., kJ	Compound	Heat of formation kJ/mole
$Fe(OH)SO_4$			
$2\,Fe(OH)SO_4 = Fe_2O(SO_4)_2 + H_2O$	96	$Fe(OH)SO_4$	−1367
$Fe_2O(SO_4)_2 = Fe_2O_3 + 2\,SO_3$	539	$Fe_2O(SO_4)_2$	−2399
$Fe_2O(SO_4)_2$			
$Fe_2O(SO_4)_2 = Fe_2O_3 + 2\,SO_3$	527		

ΔH was calculated from the heat of dehydration of iron(II) sulphate heptahydrate, and the heat of oxidation to $Fe_2O(SO_4)_2$ from the DTA curves. The heat of formation of $FeSO_4 \cdot 7\,H_2O$ was taken from the earlier work [15]. The heat of formation of H_2O was taken from the literature [16]. The heat of formation of $Fe_2O(SO_4)_2$ was calculated as follows:

$$\Delta H_{f298}Fe_2O(SO_4)_2 = \Delta H_{298} + 2(\Delta H_{f298}FeSO_4 \cdot 7\,H_2O) + \\ + 1/2\,(\Delta H_{f298}O_2) - 14\,(\Delta H_{f298}H_2O) \quad (6)$$

$$\Delta H_{298} = 334.4 \text{ kJ/mole}, \quad \Delta H_{f298}FeSO_4 \cdot 7\,H_2O = -3057.0 \text{ kJ/mole}$$

$$\Delta H_{f298}H_2O = -241.6 \text{ kJ/mole}, \quad \Delta H_{f298}O_2 = 0$$

Therefore,

$$\Delta H_{f298}Fe_2O(SO_4)_2 = 334.4 - 6114.0 + 0 + 3382.4 = -2397.2 \text{ kJ/mole.}$$

The heat of decomposition, ΔH, of the hydroxysulphate was taken to calculate $\Delta H_{f298}Fe(OH)SO_4$ as follows:

$$2\,Fe(OH)SO_4 \xrightarrow{\Delta H} Fe_2O(SO_4)_2 + H_2O \quad (1)$$

$$2\,(\Delta H_{f298}Fe(OH)SO_4) = \Delta H_{f298}Fe_2O(SO_4)_2 + \Delta H_{f298}H_2O - \Delta H_{298} \quad (7)$$

$$\Delta H_{f298}Fe_2O(SO_4)_2 = -2397.2 \text{ kJ/mole}$$

$$\Delta H_{f298}H_2O = -241.6 \text{ kJ/mole}$$

$$\Delta H_{298} = 96.9 \text{ kJ/mole}$$

Therefore,

$$2\,(\Delta H_{f298}Fe(OH)SO_4) = -2397.2 - 241.6 - 96.9 = -2735.8 \text{ kJ}$$

or,

$$\Delta H_{f298}Fe(OH)SO_4 = -1367.9 \text{ kJ/mole}.$$

The decomposition of the hydroxysulphate involves two steps: dehydration to the oxysulphate with the liberation of water (Eqn. 1), and the decomposition of the oxysulphate to iron(III) oxide and sulphur oxides (Eqn. 2). From Table 4 it will be seen that the oxysulphate formed as an intermediate during the thermal decomposition of the hydroxysulphate has a heat of decomposition close to that of the oxysulphate prepared by the isothermal method, confirming that the oxysulphate is formed as an intermediate during the thermal decomposition of the hydroxysulphate.

In conclusion, it may be said that the hydroxysulphate decomposes to the oxysulphate and water. The oxysulphate decomposes to iron(III) oxide and sulphur oxides. No intermediate is formed during the decomposition of the oxysulphate.

When the oxysulphate is the starting material, it decomposes directly to iron(III) oxide and sulphur oxides. These conclusions hold as far as dynamic thermal decomposition is concerned. During isothermal decomposition, however, the hydroxysulphate decomposes to the oxysulphate, which in turn decomposes simultaneously to iron(III) sulphate and iron(III) oxide. Iron(III) sulphate is therefore an intermediate in the thermal decomposition of the oxysulphate under isothermal conditions. Thus, the decomposition of the basic salts is determined by the experimental conditions.

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RÉSUMÉ — On a effectué, dans de l'air la décomposition thermique de l'hydroxysulphate et oxysulphate de fer. Entre conditions dynamiques, l'hydroxysulphate se décompose en oxysulphate qui, de sa part, se décompose en oxyde de fer(III) et oxydes de soufre. L'oxysulphate se décompose directement en oxyde de fer(III) et oxydes de soufre. On a calculé les chaleurs de décomposition et les chaleurs de formation des deux sulphates basiques.

ZUSAMMENFASSUNG — Die thermische Zersetzung von Eisenhydroxysulfat und -oxysulfat wurde in Luft durchgeführt. Unter dynamischen Bedingungen wird das Hydroxysulfat zu Oxysulfat zersetzt, welches seinerseits zu Eisen(III)oxiden und Schwefeloxiden zersetzt wird. Das Oxysulfat wird unmittelbar zu Eisen(III)oxid und Schwefeloxiden zersetzt. Die Zersetzungswärmen und die Bildungswärmen der zwei basischen Sulfate wurden berechnet.

Резюме — Проведено термическое разложение гидрокси- и оксисульфатов железа в атмосфере воздуха. В динамических условиях гидроксисульфат разлагается до оксисульфата, который в свою очередь разлагается до окиси железа(III) и окислов серы. Оксисульфат разлагается прямо до окиси железа(III) и окислов серы. Вычислены теплоты разложения и теплоты образования двух основных сульфатов.