THERMAL ANALYSIS OF FERROUS SULPHATE HEPTAHYDRATE IN AIR

II. THE OXIDATION-DECOMPOSITION PATH

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The thermal decomposition of ferrous sulphate heptahydrate was carried out in air under dynamic and isothermal conditions. The intermediate phases were identified by chemical analysis and an X-ray technique. Ferrous sulphate heptahydrate is converted to tetrahydrate and monohydrate, but this conversion is accompanied by oxidation. $Fe(OH)SO_4$ and $Fe_2O(SO_4)_2$ are formed as oxidation products, and the latter decomposes to ferric oxide directly and/or through $Fe_2(SO_4)_3$.

The oxidation-decomposition of ferrous sulphate heptahydrate is a diffusion-controlled process [1] and depends on various experimental parameters such as particle size, amount of the sample, thickness of the sample layer, heat-flow through the sample, etc. An account of the work done in this connection by various workers was given earlier in Part I of this paper [2]. In the present communication we report our results on the oxidation-decomposition path of ferrous sulphate heptahydrate when heated in air under controlled experimental conditions.

Experimental

Materials: Ferrous sulphate heptahydrate, as well as intermediates such as $FeSO_4 \cdot 4\,H_2O$, $FeSO_4 \cdot H_2O$, $Fe(OH)SO_4$ and $Fe_2O(SO_4)_2$, were prepared and analyzed as described earlier [2].

Apparatus: Dynamic thermal analysis studies were carried out using a derivatograph supplied by Metrimpex, Hungary. It records simultaneously the DTA, DTG, TG and T curves.

The furnace used for isothermal studies was of local make with a temperature control within $\pm 5°$ of the desired value.

A Philips X-ray unit utilizing the photographic technique was used to obtain the X-ray diffraction data.

Procedure

Dynamic thermal analysis: Two types of platinum sample holders were used: crucible (10 mm diameter and 18 mm height) and multiplate sample holder (four plates arranged above each other, of 19 mm diameter and 1.5 mm height). About

900 mg sample was filled in the crucible by gently tapping a few times, and 200 mg was evenly spread on the multiplate. The investigations were carried out from ambient temperature to 1000°, using the normal heating rate of 10°/min.

Isothermal analysis: Isothermal studies were carried out in dishes. For studies up to 300°, flat-bottomed glass dishes of 26 mm height, 36 mm diameter and 2 mm thickness were used. For temperatures above 300°, silica dishes of 15 mm height, 45 mm diameter and 3 mm thickness were used. The material (about 1 g) was spread evenly and placed in the furnace heated to the desired temperature. The samples were heated for several hours and analyzed.

Results and discussion

Typical thermal curves are shown in Figs 1 and 2, and the thermal and weight loss data are presented in Tables 1 and 2. Results of isothermal studies are given in Table 3 and the corresponding X-ray and analytical data are shown in Tables 4 and 5, respectively.
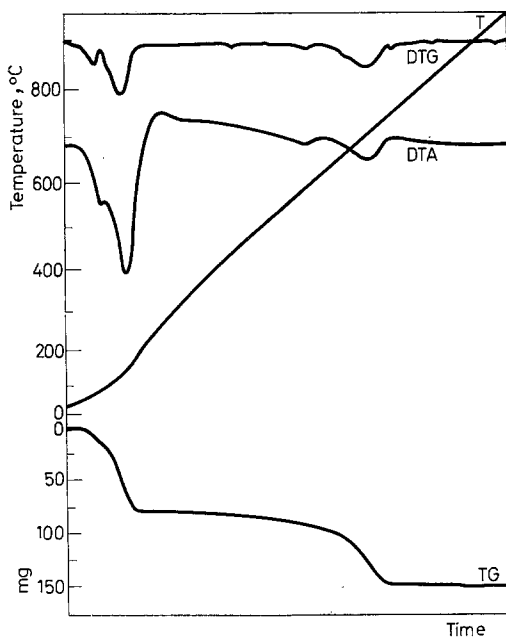

Fig. 1. Thermoanalytical curves of $FeSO_4 \cdot 7 H_2O$ using crucibles

Dynamic thermal analysis

Safiullin et al. [3], in their studies on the thermochemical conversion of analytical reagent grade $FeSO_4.7 H_2O$ in air, detected the first endotherm in the DTA curve at 68° with a corresponding weight loss of 2.5% from the TG curve, instead

of the 19.4% expected theoretically for expulsion of 3 water molecules. Nonetheless, X-ray diffraction data identified $FeSO_4.4\,H_2O$. The inability of TG to identify tetrahydrate formation was attributed by these authors to fusion of the specimen, resulting in the retention of liberated but unvolatilized water in $FeSO_4.4\,H_2O$. Bristoti and co-workers [4] used a derivatograph to investigate the effect of heating reagent grade $FeSO_4.7\,H_2O$ at two heating rates in air, *viz.* 10° and 0.5°/min. Although the latter TG curve indicated inflexion, the authors did not report the formation of tetrahydrate.

Fig. 2. Thermoanalytical curves of $FeSO_4 \cdot 7\,H_2O$ using multiple sampleholders

Because of the considerable diversity of views, we carried out our studies in two different types of sample holders (crucibles and multiplate sample holders). From Figs. 1 and 2 it will be seen that the shapes of the two curves are different for crucibles and multiplate sample holders. The most striking difference is in the oxidation. In crucibles the exothermic peak occurs between 540 and 600°, whereas in multiplate sample holders it occurs at 260°. The occurrence of an oxi-

dation peak at higher temperatures in crucibles may be attributed to the evolution of water vapour which to a considerable extent prevents diffusion of oxygen into the substance. In the case of multiplate sample holders the large surface area allows diffusion of oxygen even at lower temperatures. In both cases tetrahydrate formation could not be accounted for. This may be due to fusion of the sample

Table 1

Thermal data on the decomposition of $FeSO_4 \cdot 7H_2O$ in crucibles and multiplate sample holders in air (cf. Figs 1 and 2)

| S. No.	Event	Temperature, °C	
		Crucibles	Multiplate sample holders
1.	Stability of $FeSO_4 \cdot 7H_2O$	up to 60	up to 60
2.a.	Decomposition to tetrahydrate	110*	60
b.	DTG/DTA peak (endo)	—	80/90
c.	Completion of decomposition	—	95
3.a.	Stability of tetrahydrate	—	**
b.	Decomposition to monohydrate	120	95
c.	DTG/DTA peak (endo)	175/190	140/150
d.	Completion of decomposition	230	160
4.a.	Stability of monohydrate	***	**
b.	Decomposition of monohydrate	230	—
c.	Oxidation of monohydrate to $Fe(OH)SO_4$	—	160—310
d.	DTG/DTA peak (endo)	370/370	—
e.	Completion of decomposition	380	—
5.a.	Stability of anhydrous salt	380—505	—
b.	Stability of $Fe(OH)SO_4$	—	**
c.	Oxidation of anhydrous salt	505	—
d.	Decomposition of $Fe(OH)SO_4$ to $Fe_2O(SO_4)_2$	—	310—600
e.	DTG/DTA peak (exo, endo)	570—600/550, 590 (exo)	580/580 (endo)
f.	Completion of decomposition	—	600
g.	Completion of oxidation	610	—
6.a.	Stability of $Fe_2O(SO_4)_2$	610—660	**
b.	Decomposition to Fe_2O_3	660	600
c.	DTG/DTA peak (endo)	800/810	700/700
d.	Completion of decomposition	830	720

    * inflection
   ** not stable
 *** not stable, decomposes slowly to anhydrous salt.

in the case of crucibles, and quick removal of water simultaneously with oxidation in the case of multiplate sample holders. The thermal data obtained from experiments in crucibles (cf. Tables 1 and 2) indicate the formation of tetrahydrate,

monohydrate, anhydrous compound, oxosulphate and finally ferric oxide. There is no endothermic peak corresponding to the reaction:

$$2 \, Fe(OH)SO_4 = Fe_2O(SO_4)_2 + H_2O \tag{1}$$
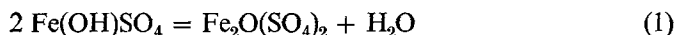
and it appears that the anhydrous ferrous sulphate is oxidized directly to the oxo compound, $Fe_2O(SO_4)_2$. The experimental data on multiplate sample holders (cf. Tables 1 and 2) indicate that the oxidation-decomposition process assumes

Table 2

Weight loss data for the thermal decomposition of $FeSO_4 \cdot 7H_2O$ in crucibles and multiplate sample holders in air (cf. Figs 1 and 2)

S. No.	Step	Weight loss/gain, %			
		Calculated		Observed	
		crucibles	multiplate sample holders	crucibles	multiplate sample holders
1.	$FeSO_4 \cdot 7H_2O = FeSO_4 \cdot 4H_2O + 3 \, H_2O$	-19.4	-19.4	-2.2	-7.5
2.	$FeSO_4 \cdot 7H_2O = FeSO_4 \cdot H_2O + 6 \, H_2O$	-38.9	-38.9	-37.5	-38.7
3.	$FeSO_4 \cdot H_2O = FeSO_4 + H_2O$	-10.6	—	-10.4	—
4.	$2 \, FeSO_4 \cdot 7H_2O + 1/2O_2 = 2 \, Fe(OH)SO_4 + {} + 13 \, H_2O$	—	-39.2	—	-41.0
5.	$2 \, FeSO_4 + 1/2O_2 = Fe_2O(SO_4)_2$	$+5.3$	—	$+1.5*$	—
6.	$2 \, FeSO_4 \cdot 7H_2O + 1/2O_2 = Fe_2O(SO_4)_2 + {} + 14 \, H_2O$	—	-42.5	—	-47.5
7.	$Fe_2O(SO_4)_2 = Fe_2O_3 + 2 \, SO_3**$	-50.0	-50.0	-50.7	-47.6
8.	$2 \, FeSO_4 \cdot 7H_2O + 1/2O_2 = Fe_2O_3 + {} + 14 \, H_2O + 2 \, SO_3**$	-71.2	-71.2	-71.7	-72.5

* Part of the oxidation takes place along, with dehydration.
** Decomposes to SO_2 and O_2.

a more complex nature owing to overlapping reactions. Individual steps, therefore, could not be explained. However, an approximate analysis of the thermal data suggests that both $Fe(OH)SO_4$ and $Fe_2O(SO_4)_2$ are formed in addition to $FeSO_4 \cdot 4 \, H_2O$ and $FeSO_4 \cdot H_2O$. In both cases the oxosulphate decomposes to ferric oxide:

$$Fe_2O(SO_4)_2 = Fe_2O_3 + 2 \, SO_3 \tag{2}$$

Isothermal studies

Data on the isothermal decomposition of ferrous sulphate heptahydrate and the X-ray diffraction of intermediate compounds are given in Tables 3 and 4. These results indicate that the tetrahydrate is formed at 42° but is accompanied

by slight (1.8%) oxidation. The formation of monohydrate is accompanied by considerable oxidation. As the temperature increases, oxidation also increases; at 120–300° it is complete and the compound formed is $Fe(OH)SO_4$. On further heating, $Fe(OH)SO_4$ decomposes (350°) and at about 400° the composition cor-

Table 3

Isothermal decomposition of $FeSO_4 \cdot 7H_2O$

S. No.	Temperature, °C	Heating time, hours	Weight loss, %	Iron in product, %	Oxidation, %	Proposed intermediate compounds*
1.	42	50	19.20	25.80	1.8	$FeSO_4 \cdot 4H_2O + FeSO_4 \cdot H_2O +$ $Fe(OH)SO_4$
2.	50	50	32.50	31.20	5.7	$FeSO_4 \cdot 4H_2O + FeSO_4 \cdot H_2O +$ $+ Fe(OH)SO_4$
3.	60	48	36.00	32.10	19.5	$FeSO_4 \cdot H_2O + FeSO_4 \cdot 4H_2O +$ $+ Fe(OH)SO_4$
4.	74	50	36.10	32.30	54.2	$Fe(OH)SO_4 + FeSO_4 \cdot H_2O +$ $+ FeSO_4 \cdot 4H_2O$
5.	90	40	36.80	33.00	91.0	$Fe(OH)SO_4 + FeSO_4 \cdot H_2O +$ $+ FeSO_4 \cdot 4H_2O$
6.	120	35	37.20	33.02	99.4	$Fe(OH)SO_4 + FeSO_4 \cdot H_2O +$ $+ FeSO_4 \cdot 4H_2O$
7.	250	25	41.40	33.06	99.7	$Fe(OH)SO_4 + FeSO_4 \cdot H_2O$
8.	270	24	42.00	33.07	100.0	$Fe(OH)SO_4$
9.	300	23	42.30	33.08		$Fe(OH)SO_4$
10.	330	24	42.50	33.09		$Fe(OH)SO_4$
11.	350	24	43.50	33.50		$Fe(OH)SO_4 + Fe_2O(SO_4)_2$
12.	380	23	44.00	33.64		$Fe(OH)SO_4 + Fe_2O(SO_4)_2$
13.	400	22	44.70	33.90		$Fe_2O(SO_4)_2 + Fe(OH)SO_4$
14.	410	20	45.00	34.80		$Fe_2O(SO_4)_2$
15.	420	20	45.28	35.00		$Fe_2O(SO_4)_2$
16.	440	21	46.00	35.50		$Fe_2O(SO_4)_2 + Fe_2(SO_4)_3 + Fe_2O_3$
17.	500	14	49.30	38.00		$Fe_2(SO_4)_3 + Fe_2O(SO_4)_2 + Fe_2O_3$
18.	550	6	71.20	71.00		Fe_2O_3

* First compound represents major component followed by those in decreasing order. Theoretical values for weight loss % and iron % respectively: $FeSO_4 \cdot 4H_2O$ (19.4, 24.95); $FeSO_4 \cdot H_2O$ (38.9, 32.88); $Fe(OH)SO_4$ (42.1, 33.08); $Fe_2O(SO_4)_2$ (45.3, 34.94); Fe_2O_3 (71.2, 69.94); $Fe_2(SO_4)$ (42.47, 27.95).

responds to $Fe_2O(SO_4)_2$. The latter is stable over only a narrow range (400–420°). It decomposes above 420°. The X-ray data (Table 4) indicate that $Fe_2O(SO_4)_2$ decomposes to Fe_2O_3 directly and/or though the intermediate $Fe_2(SO_4)_3$.

From the foregoing discussion it is thus evident that ferrous sulphate heptahydrate is converted to intermediate tetrahydrate and monohydrate, but this conversion is accompanied by oxidation or basic compound formation. If the

Table 4

X-ray diffraction data (samples given in Table 3)

Temperature, °C	$^od'$ values with probable assignments
74	4.82 (2); 3.45 (2); 3.28 (5); 2.58 (2); 2.52 (2); 2.0 (2.5).
90	4.95 (2); 4.79 (5); 3.43 (2); 3.26 (5); 3.16 (2); 2.58 (2); 2.5 (2); 2.0 (2.5); 1.64 (5); 1.59 (5); 1.54 (3).
120	4.75 (5); 3.59 (5); 3.26 (5); 3.21 (5); 2.57 (2); 2.29 (5); 2.0 (2.5); 1.84 (5); 1.6 (5); 1.56 (5).
300	4.74 (5); 3.55 (5); 3.26 (5); 2.33 (5); 2.04 (5); 1.99 (5); 1.83 (5); 1.63 (5); 1.59 (5); 1.56 (5).
380	4.74 (5); 3.56 (5, 6); 3.25 (5); 2.49 (6); 2.28 (6); 1.98 (5); 1.83 (5); 1.63 (5); 1.59 (5); 1.55 (5).
420	4.98 (6); 4.36 (6); 3.57 (6); 3.19 (6); 3.14 (6); 2.72 (6); 2.49 (6); 2.39 (6); 2 28 (6); 1.84 (5, 6, 7).
440	5.98 (4); 4.35 (6); 3.66 (7); 3.56 (6); 2.28 (6); 1.99 (4); 1.85 (4, 7); 1.7 (7); 1.61 (4, 7); 1.49 (4, 7); 1.46 (4, 7).
500	5.98 (4); 4.35 (6); 3.61 (4); 3.25 (6); 3.0 (4); 2.73 (6); 2.53 (7); 2.4 (6); 2.25 (4); 1.86 (4); 1.71 (4); 1.57 (4).
Sample 1*	5.47 (1); 4.84 (8, 2); 3.98 (1); 3.41 (1, 2); 2.75 (1).
Sample 2*	4.83 (2); 3.44 (2); 3.28 (5); 2.52 (2); 2.23 (2); 1.99 (1, 2); 1.94 (2); 1.72 (2); 1.69 (2); 1.59 (2); 1.45 (1).

* Samples 1 and 2 are $FeSO_4 \cdot 4H_2O$ and $FeSO_4 \cdot H_2O$ prepared by procedure given earlier [2]. Note: — The numbers in parenthesis in column 2 represent the following compounds along with reference to ASTM cards: (1) $FeSO_4 \cdot 4H_2O$: 1—201; (2) $FeSO_4 \cdot H_2O$: 1—612; (3) $FeSO_4$: 1—703; (4) $Fe_2(SO_4)_3$: 18—652; (5) $Fe(OH)SO_4$: 21—428; (6) $Fe_2O(SO_4)_2$: new phase; (7) Fe_2O_3 : 13—534; (8) $FeSO_4 \cdot 7H_2O$: 1—255.

Table 5

Composition of the isolated intermediate compounds

S. No.	Intermediate compound	Free acid, moles	Sulfate, %		Iron, %		Water molecules	
			Cal-culated	Ob-served	Calcu-lated	Ob-served	Calcu-lated	Ob-served
1.	$FeSO_4 \cdot 7H_2O$	6.3×10^{-5}	34.55	34.53	20.10	20.10	7	7.03
2.	$FeSO_4 \cdot 4H_2O$	1.2×10^{-4}	42.86	42.76	24.95	24.90	4	4.09
3.	$FeSO_4 \cdot H_2O$	1.0×10^{-3}	56.47	56.29	32.88	32.70	1	1.03
4.	$Fe(OH)SO_4$	1.6×10^{-3}	56.81	56.80	33.08	33.07	0.5	0.51
5.	$Fe_2O)SO_4)_2$	5.0×10^{-3}	60.00	59.75	34.94	35.06		

intermediate hydrates are to be isolated in pure orm, special methods [2] must be employed to prevent their oxidation. During the decomposition of ferrous sulphate heptahydrate, both $Fe(OH)SO_4$ and $Fe_2O(SO_4)_2$ are formed as well-

defined intermediates. The compound $Fe(OH)SO_4$ is stable over a wider range of temperature $(120-330°)$ than the oxo compound $(400-420°)$. This may be the reason why earlier workers could not identify this compound during dynamic studies.

<p style="text-align:center">*</p>

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RÉSUMÉ — La décomposition thermique dans l'air du sulfate de fer(II) heptahydraté a été étudiée en conditions dynamiques et isothermes. Les phases intermédiaires ont été identifiées par analyse chimique et par rayons X. Le sulfate de fer(II) heptahydraté se transforme en tétrahydrate et en monohydrate mais cette conversion s'accompagne d'une oxydation. Il se forme $Fe(OH)SO_4$ et $Fe_2O(SO_4)_2$ comme produits d'oxydation et ce dernier se décompose en oxyde de fer(III) directement ou quelquefois avec formation intermédiaire de $Fe_2(SO_4)_3$.

ZUSAMMENFASSUNG — Die thermische Zersetzung von Eisen(II)sulfat Heptahydrat wurde in Luft unter dynamischen und isothermen Bedingungen durchgeführt. Die Intermediärphasen wurden durch chemische Analyse und Röntgentechnik identifiziert. Eisen(II)sulfat Heptahydrat wird in Tetrahydrat und Monohydrat überführt, doch wird diese Umwandlung durch eine Oxidation begleitet. $Fe(OH)SO_4$ und $Fe_2O(SO_4)_2$ werden als Oxidationsprodukte gebildet und letzteres wird unmittelbar und/oder über $Fe_2(SO_4)_3$ zu Eisen(III)oxid zersetzt.

Резюме — Проведено термическое разложение гептагидрата сульфата железа(II) в воздушной атмосфере в динамических и изотермических условиях. С помощью химического анализа и рентгенографии идентифицированы промежуточные фазы. Гептагидрат сульфата железа(II) превращается до тетрагидрата и моногидрата с сопровождающимся при этом окислении. В качестве продуктов окисления образуются $Fe(OH)SO_4$ и $Fe_2O(SO_4)_2$. Последний продукт разлагается до окиси железа(III) прямо или через образование $Fe_2(SO_4)_3$.