A Study of the Thermo-oxidation of Fe(II) in $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

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The thermo-oxidation in air of Fe(II) and weight loss of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ has been measured as a function of time in the temperature range 43 to 170 °C. The analysis of the results suggests the following reaction mechanism: by heating, the heptahydrate loses water resulting in a mixture of the tetra- and monohydrate. Only the latter can be oxidized. The activation energy for oxidation is found to be about $3.5 \times 10^4 \text{ J mol}^{-1}$.

I. INTRODUCTION

When $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is heated in air two processes take place: thermal decomposition and oxidation. Kohler,¹ studying the thermal decomposition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ obtained the following hydrate phases when heating isobarically at 20 Torr: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, FeSO_4 at 22, 30, 165, and higher than 240 °C, respectively.

Safiullin,² using X-ray and IR spectroscopy found that in the 134–309 °C range the monohydrate is oxidized to $\text{Fe}(\text{OH})\text{SO}_4$ by the reaction

X-Ray analysis revealed the presence of both the basic salt and the anhydrous ferrous sulfate at 312 °C. On further heating they are oxidized to $\text{Fe}_2\text{O}(\text{SO}_4)_2$.

Gallagher,³ using weight loss data in the region 150 to 500 °C concluded that in O_2 atmosphere, Fe(II) was converted to Fe(III) before the sulfate ion decomposed, whereas in N_2 atmosphere the conversion occurred simultaneously with the first step of the sulfate

decomposition. Two pathways were suggested leading to the formation of $\text{Fe}_2\text{O}(\text{SO}_4)_2$.

Kamel,⁴ using X-ray and chemical analysis investigated the intermediate products of the thermal decomposition of ferrous sulfate heptahydrate in a current of air. The monohydrate undergoes dehydration followed by oxidation, combined hydrolysis and oxidation to $\text{Fe}_2\text{O}(\text{SO}_4)_2$ and $\text{Fe}(\text{OH})\text{SO}_4$, respectively.

Wanek and Knob⁵ showed that the weight loss is strongly temperature dependent below 220 °C.

The purpose of the present work was to study in some detail the processes which take place when $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is heated in air using weight loss and oxidation measurements.

II. EXPERIMENTAL PROCEDURE

1. Materials. "Mercks Reagenzien"- $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ crystalline powder with mean grain size 0.1 mm³ and molecular weight 278.03, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ crystals grown to about 100 mg, "standard solution" made of 0.8 N H_2SO_4 and 1 mM NaCl.⁶ All chemicals were of grade *p.a.* For the temperature measurements a PYE scalamp galvanometer with copper-constantan thermocouple was used. The optical densities were measured using a "Carl Zeiss" spectrophotometer PMQII/M4QIII.

2. Procedure. Samples of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were carefully weighed ($X \approx 25 \text{ mg}$), placed in open glass boats and heated in a copper tube furnace.⁷ This furnace has a connection to the source of the desired gas (O_2 , N_2 or air). The desired temperature was obtained by the use of a heating element, controlled by a thermo regulator. When air was not used, a stream of the desired gas was passed through the furnace for about 15 h at room temperature to get rid of undesired gases.

The sample was removed from the furnace, weighed and then dissolved in *V* ml of the standard solution. Values for the concentration

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Table 1. Values and formulae used for the molar extinction coefficients in $\text{mol}^{-1} \text{cm}^{-1}$. The temperature of the measured solution, τ , in $^{\circ}\text{C}$.

λ (nm)	ϵ_{III}	ϵ_{II}
304	$2121\{1 + 0.007(\tau - 20)\}$	1
275	1830	1
224	$4565\{0.0015(\tau - 25) + 1\}$	20

of Fe(III) were obtained by the measurement of optical densities.

The optical density $^{\circ}\text{OD}_{\text{rel}}$ of the resulting solution relative to that of the standard solution is composed of the optical densities of the two components Fe(II) and Fe(III), *i.e.*

$$\text{OD}_{\text{rel}} = [\epsilon_{\text{II}}\{\text{Fe(II)}\} + \epsilon_{\text{III}}\{\text{Fe(III)}\}]d \quad (1)$$

where ϵ_{II} and ϵ_{III} are the molar extinction coefficients of Fe(II) and Fe(III), respectively, and $d=1$ cm, is the light path length in the solution. The concentration of Fe(III) is then given by:

$$\{\text{Fe(III)}\} = \frac{\text{OD}_{\text{rel}} - \{\text{Fe(II)}\}\epsilon_{\text{II}}d}{d(\epsilon_{\text{III}} - \epsilon_{\text{II}})} \quad (2)$$

Here $\{\text{Fe(II)}\}_0 = X/MV$, where M is the molecular weight of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Values and formulae used for the molar extinction coefficients in units of $\text{mol}^{-1} \text{cm}^{-1}$ are given in Table 1,^{10,11} where $\tau(^{\circ}\text{C})$ is the temperature of the measured solution. Uncertainties in measurements were: for relative concentration, $\pm(1.2\% + 5 \times 10^{-4})$; for temperature, $\pm 2\%$; and for weighing, $\pm 0.6\%$.

Fig. 1. The variation of the weight of the sample with time at various temperatures. $\blacktriangle$ 43°C ; $\circ$ 54°C ; $\triangle$ 67°C ; $\square$ 77°C ; $\bullet$ 85°C ; $\blacksquare$ 92°C ; $\times$ 170°C .

Table 2. Average water concentration, per molecule and fraction monohydrate, $f = \{\text{FeSO}_4 \cdot \text{H}_2\text{O}\}_{t=0} / \{\text{Fe(II)}\}_0$, at various temperatures, τ ($^{\circ}\text{C}$).

τ ($^{\circ}\text{C}$)	n (H_2O mol)	f
43	3.6	0.13
54	2.6	0.46
67	1.8	0.74
77	1.6	0.79
85	1.3	0.90
92	1.15	0.95
170	1.15	0.95

III. RESULTS AND DISCUSSION

The weight of the samples (normalized to 25 mg) at various temperatures in ordinary air is plotted *versus* time in Fig. 1. The figure shows that within a relative short time the weight reaches a limiting value. At 54°C this time is about 3 h and it decreases with increasing temperature. This indicates that the composition of the crystals do not change appreciably after that time and within the time limit of the experiments. Assuming the weight-loss to be entirely due to H_2O , we estimated the values of the water concentration $\{\text{H}_2\text{O}\}$ to be those given in Table 2. X-Ray analysis shows the presence

Fig. 2. Oxidation of Fe(II) with time at various temperatures. Symbols as in Fig. 1.

Table 3. Results from oxidation experiments, where $Y = \{[\text{Fe(III)}]/[\text{Fe(II)}]_0\} \times 10^3$.

Time h	Y	Time h	Y	Time h	Y	Time h	Y	Time h	Y	Time h	Y	Time h	Y
$\tau = 43^\circ\text{C}$		$\tau = 54^\circ\text{C}$		$\tau = 67^\circ\text{C}$		$\tau = 77^\circ\text{C}$		$\tau = 85^\circ\text{C}$		$\tau = 92^\circ\text{C}$		$\tau = 170^\circ\text{C}$	
1	4	2.1	14	2	32	2	139	1	114	0.25	23	0.5	587
2.5	12	3	17	4	73	3	201	1.5	185	0.5	122	1	722
3.5	12	4	20	5	87	4	213	2	200	1	196	1.5	778
5	9	7.5	43	9	158	5	282	3	270	2	325	3	833
8	17	13	92	14	241	8	339	4	301	3	395	4	846
16	11	15	105	17	280	10	423	5	357	4	409	5	852
20	19	18	93	20.25	340	16	555	6	383	6	528	6	824
24	15	26	98	24	400	19	610	8.5	482	9	582	14	861
						21	635	10	513	16	732	17	881
						23	673	16.5	660	20	750	24	873
						24	667	21	715	21.5	783		
								24	738	24	781		

of only tetrahydrate and monohydrate; consequently the fraction of the monohydrate at the beginning of oxidation was estimated and given in Table 2.

Results from the oxidation experiments are given in Table 3. In Fig. 2, values for the ratio $[\text{Fe(III)}]/[\text{Fe(II)}]_0 \times 10^3$ with ordinary air as oxidant are plotted *versus* time for the temperatures 43, 54, 67, 77, 85, 92, and 170°C .

The figure shows that (1) no oxidation takes place below 54°C , and (2) at each temperature the oxidation yield increases with time and reaches an apparent limiting value which increases with increasing temperature.

In a separate experiment with a current of

Fig. 3. Comparison between oxidation curves in ordinary air and in saturated air at $\tau = 54^\circ\text{C}$. $\circ$ Ordinary air; $\triangle$ saturated air.

about $30 \text{ dm}^3 \text{ h}^{-1}$ of pure and wet N_2 instead of air we observed no oxidation to take place. Hence O_2 in the air must be the oxidant. The species which can be oxidized are $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$, and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ which have been shown to be present in the temperature range we are considering.

To study the possibility of the heptahydrate oxidation, samples were heated at 54°C in a current of $180 \text{ dm}^3 \text{ h}^{-1}$ of air saturated with H_2O , as obtained by passing the air through water at $\tau = 54^\circ\text{C}$. Under these conditions only the heptahydrate is present and no oxidation was shown to take place whereas in ordinary air heated to 54°C the oxidation is not negligible. A comparison between the results from these two experiments is shown in Fig. 3.

That the crystals have to loose water before they can be oxidized was further substantiated by the fact that when large crystals were used, the oxidation rate remained low for a longer time than when smaller crystals were used as shown in Fig. 4.

According to weight loss measurements, Fig. 1 and Table 2, and the increase of the oxidation rate with increasing temperature, one suggests that neither tetrahydrate can be oxidized.

The oxidation of the monohydrate may proceed as follows:

Fig. 4. Comparison between oxidation curves for ordinary powder and for bigger crystals at $\tau = 67^\circ\text{C}$. Δ Ordinary powder, $\circ$ crystal.

The oxidation rate is then given by:

$$\frac{d\{\text{Fe(III)}\}}{dt} = k_1\{\text{O}_2\}^\alpha\{\text{FeSO}_4\cdot\text{H}_2\text{O}\}^\beta - k_2\{\text{H}_2\text{O}\}^\gamma\{\text{Fe(OH)SO}_4\}^\delta \quad (4)$$

where k_1 is the oxidation rate constant, k_2 is the rate of the reverse reaction; α , β , γ , and δ are the reaction orders relevant to the various species.

To study the reverse reaction, samples, which had been oxidized for 24 h at 92°C were heated for another 24 h and at the same temperature in a current of $60\text{ dm}^3\text{ h}^{-1}$ of nitrogen saturated with water. The amount of Fe(III) did not change with time. Also X-ray analysis showed no variation in the composition with time. This suggests that the reverse reaction can be ignored. If this is the case, then, according to eqn. (4), all Fe(II) in the sample should be oxidized to Fe(III). However, according to Fig. 2, it is seen that only a fraction of Fe(II) is oxidized and this fraction increases with increasing temperature. One reason might be that the concentration $\{\text{O}_2\}$ in the crystals decreases to zero, i.e. the value of the rate constant for the diffusion of O_2 into the crystals goes to

zero after a certain time. Such effect could be due to the formation of a crust of oxides on the surface of the crystals. This was shown to be the case by the following two sets of experiments:

(1) For a specimen heated and oxidized in ordinary air for 24 h. X-ray analysis revealed the presence of ferrous sulfate monohydrate and a mixture of oxides.

(2) Scanning microscopic examination of sections cut from a crystal heated to 85°C for 24 h shows an outer crust around the original crystal. A comparison of the spectrum of the inner and outer layers indicates difference in the composition of these layers. Hence at the end of oxidation there is a crust of oxides around an inner layer of ferrous sulfate (mono- and tetrahydrate). The formation of such crust may affect the reaction rate constant; therefore to avoid complications we shall analyze the oxidation rate at the beginning of the process where $\{\text{Fe(III)}\}$ is negligible and $\{\text{O}_2\}$ may be assumed to be constant. Assuming first order reaction, we obtain.

$$\left(\frac{d\{\text{Fe(III)}\}}{dt}\right)_{t=0} = K\{\text{FeSO}_4\cdot\text{H}_2\text{O}\}_{t=0} \quad (5)$$

where $\{\text{FeSO}_4\cdot\text{H}_2\text{O}\}_{t=0}$ is the concentration of the monohydrate at the beginning of the oxidation (and after dehydration). The concentration of $\text{FeSO}_4\cdot\text{H}_2\text{O}$ does in fact vary with time due to the following process:

Fig. 5. Relationship between rate constant K , $(=k_1\{\text{O}_2\}^{1/4})$, and absolute temperature T .

However, according to the results obtained above from weightloss measurements this process is fast relative to the oxidation process except perhaps at $\tau = 54^\circ\text{C}$. To check the effect of dehydration during oxidation, an experiment was performed in which the samples were dehydrated for 3 h in an inert atmosphere (N_2) at the desired temperature before oxidation. No significant changes in the oxidation rate were observed.

We assume now the oxidation rate constant k_1 to be proportional to $e^{-E/RT}$, where E is the activation energy for oxidation, R is the universal gas constant; and T is the absolute temperature. Then since $\{\text{O}_2\}$ is a constant the parameter K , given by $\left(\frac{d\{\text{Fe(III)}\}}{dt}\right)_{t=0}/\{\text{FeSO}_4 \cdot \text{H}_2\text{O}\}_{t=0}$ in eqn. (5), is also proportional to $e^{-E/RT}$.

Using the oxidation curves in Fig. 2, values of $(d\{\text{Fe(III)}\}/dt)_{t=0}$ have been determined by the slope of the curves at the beginning of the process and by applying $\{\text{FeSO}_4 \cdot \text{H}_2\text{O}\}_{t=0}$ values, illustrated in Table 2. The plot of $\log K$ versus $1/T$ is presented in Fig. 5. The slope of the curve corresponds to an activation energy of $(3.5 \pm 0.5) \times 10^4 \text{ J mol}^{-1}$.

CONCLUSION

In this work we have measured the oxidation rate of Fe(II) in $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in the temperature range $\tau = 43 - 170^\circ\text{C}$. At a certain temperature, the oxidation increases with time and reaches an apparent limiting value which increases with increasing temperature.

No oxidation takes place below $\tau = 54^\circ\text{C}$, also no oxidation takes place when heating the sample neither in N_2 atmosphere nor in air saturated with H_2O .

Crystals have to lose water before they can be oxidized. The oxidation rate constant is proportional to $e^{-E/RT}$. The activation energy of oxidation is found to be $3.5 \times 10^4 \text{ J mol}^{-1}$.

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