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THERMAL ANALYSIS OF FERROUS SULPHATE HEPTAHYDRATE IN AIR

PART I. SOME GENERAL REMARKS AND METHODS

M. S. R. Swamy, T. P. Prasad and B. R. Sant

Regional Research Laboratory, Bhubaneswar-751013, India

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The literature on thermal analysis of ferrous sulphate heptahydrate in air is reviewed. The oxidation-decomposition of ferrous sulphate heptahydrate is a complex function of experimental conditions. Some general methods including those developed by the authors for the purpose of analyzing various intermediates encountered during the oxidation-decomposition of the heptahydrate are presented and discussed.

Large quantities of ferrous sulphate are formed during pickling of iron and steel products in sulphuric acid, manufacture of titanium dioxide from ilmenite by sulphate route and cementation of copper sulphate by scrap iron. Attention has been paid throughout the world on the utilisation of this product either in the form of liquor or solid (heptahydrate). One of the major steps involved in the utilisation of the solid is dehydration to the monohydrate or anhydrous stage after which it is roasted to get ferric oxide and oxides of sulphur. This process involves oxidation-decomposition resulting in a number of intermediate compounds. Many attempts have been made to identify the oxidation-decomposition path [1–22] and the results obtained by various authors differ widely as to the formation and nature of the intermediate compounds and their temperatures of formation.

We have taken up detailed studies on thermal analysis of ferrous sulphate heptahydrate in air with a view to understand the oxidation-decomposition path. This paper summarises the earlier findings and also gives an account of the general methods of preparation of various materials encountered in the present investigation including their analyses. Table 1 gives a summary of various intermediate compounds formed during the decomposition of hydrated ferrous sulphate in air as reported in the literature.

It is a common observation that when ferrous sulphate heptahydrate is left open to atmosphere, it tends to get slowly oxidized to yellow brown product of variable composition. It may also lose some water of crystallisation. According to the recent findings of Hassanein and Orjasaeter, the heptahydrate, as long as it retains all the molecules of water (temperature less than 54°), does not undergo oxidation [23].

When ferrous sulphate heptahydrate is heated slowly from room temperature at a programmed rate or isothermally under controlled conditions, the oxidation-

Table 1

Intermediate compounds formed during the oxidation-decomposition of ferrous sulphate heptahydrate in air

Intermediate	Temp. of formation, °C	Reference
1. $FeSO_4 \cdot 4\,H_2O$	30	20
2. $FeSO_4 \cdot H_2O$	40–90	1–4
	>90	5–8,23
	120	25
	140	10
	165	20
3. $FeSO_4 \cdot H_2O + Fe(OH)SO_4$	120	25
4. $FeSO_4$	≤ 150	26
	>240	20
5. $Fe(OH)SO_4$	215	23
	150	26
6. $Fe(OH)SO_4 + FeSO_4$	312	25
7. $Fe_2O(SO_4)_2$	450	29
	458	25
	500	11
	520	27
8. $Fe_2(SO_4)_3$	520	28
9. $Fe_{12}O_3(SO_4)_2$	475	26
10. Fe_2O_3	580 (traces)	27
	500–600	26
	760	11
	680–740	27
11. $HFeO_2$	≥ 550	26
12. $HFeO_2 \cdot nH_2O$	≥ 550	26

decomposition process can be controlled. The first product expected in all the cases is the tetrahydrate. Whereas the X-ray examination shows the presence of the tetrahydrate along with some monohydrate, TG analysis does not confirm this [24]. The failure of the weight loss measurements to identify the tetrayhydrate was attributed to its fusion so that the liberated water does not volatilize but forms a melt in which the solid phase contains tetrahydrate [24].

The ferrous sulphate tetrahydrate on further heating loses water to form the monohydrate. Simultaneously a part of the monohydrate may undergo oxidation to hydroxysulphate, $Fe(OH)SO_4$ [24]:

$$2\,FeSO_4 \cdot H_2O + 1/2\,O_2 = 2\,Fe(OH)SO_4 + H_2O \qquad (1)$$

The monohydrate may undergo transformation in any of the two ways [25, 26, 27–30] represented by Eqs (1) and (2):

$$FeSO_4 \cdot H_2O = FeSO_4 + H_2O \qquad (2)$$

It appears that the decomposition of the monohydrate depends on experimental conditions. If the decomposition is carried out at lower temperatures, more hydroxy sulphate is formed while at higher temperatures, more anhydrous sulphate is formed [29]. According to Bristoti *et al* [28] at lower heating rates of 0.5°/min. the monohydrate is oxidised completely to the hydroxy sulphate by 345° while at higher heating rates of 10°/min. the anhydrous sulphate is formed at 360°.

The anhydrous sulphate, $FeSO_4$, and the hydroxy sulphate, $Fe(OH)SO_4$, thus formed undergo oxidation and decomposition, respectively on further raising the temperature. The anhydrous sulphate is converted to the oxosulphate, $Fe_2O(SO_4)_2$, by direct oxidation:

$$2\,FeSO_4 + 1/2\,O_2 = Fe_2O(SO_4)_2 \tag{3}$$

Kamel *et al.* [27] suggest that in addition to the reaction (3) there occurs a combined hydrolysis and oxidation process as represented by:

$$FeSO_4 + FeSO_4 \cdot H_2O + 1/2\,O_2 = 2\,Fe(OH)SO_4 \tag{4}$$

While there is a general agreement that the anhydrous sulphate is transformed into the oxosulphate, $Fe_2O(SO_4)_2$, Margulius *et al* [29] claim that oxosulphate is not formed at all but the anhydrous sulphate is transformed into normal ferric sulphate, $Fe_2(SO_4)_3$:

$$6\,FeSO_4\ 1.5\,O_2 = 2\,Fe_2(SO_4)_3 + Fe_2O_3 \tag{5}$$

In their opinion the reported formation of oxosulphate by other authors is owing to the two-stage character of desulphurisation of the original sulphate and unreliable determination of the phase composition of the intermediate product.

The hydroxy sulphate decomposes on heating to the oxosulphate according to the reaction:

$$2\,Fe(OH)SO_4 = Fe_2O(SO_4)_2 + H_2O \tag{6}$$

The oxosulphate now decomposes on further heating. While majority of the workers suppose that the oxosulphate decomposes to alpha ferric oxide and sulphur oxides as represented by:

$$Fe_2O(SO_4)_2 = Fe_2O_3 + 2\,SO_3 \tag{7}$$

Kamel *et al* [27] claim that it first decomposes to ferric sulphate as follows:

$$3\,Fe_2O(SO_4)_2 = 2\,Fe_2(SO_4)_3 + Fe_2O_3 \tag{8}$$

These authors also conclude that the normal ferric sulphate does not decompose directly to ferric oxide as many authors suppose, but to another basic salt as follows:

$$6\,Fe_2(SO_4)_3 = Fe_{12}O_3(SO_4)_{15} + 3\,SO_3 \tag{9}$$

The evidence for the existence of $Fe_{12}O_3(SO_4)_{15}$ comes from the work of Walter–Levy and Quemeneur [31].

Table 2

Analysis of $FeSO_4 \cdot 7\,H_2O$

1. *Water molecules*	
Na_2CO_3 method	7.30, 7.26, 7.28
MgO method	7.04, 7.02, 7.03
Standard method	6.99
Theoretical	7.00
2. *Sulphate content* (%)	
Na_2CO_3 method	34.52, 34.56, 34.54
MgO method	34.50, 34.54, 34.52
Standard method	34.51, 34.55, 34.53
Theoretical	34.55
3. *Free acid (moles/g)*	6.3×10^{-5}
4. *Fe content* (%)	
Found	20.10
Theoretical	20.10

The oxidation-decomposition path of ferrous sulphate heptahydrate is thus a complex function of experimental conditions. As the oxidation and decomposition with the expulsion of gaseous products is a diffusion controlled phenomenon [32], the path depends on the amount of the substance, thickness of the layer, particle size, sample environment and so on. The rate of heat flow into the sample is another important factor. These factors, unless carefully controlled, may lead to erraneous conclusions as several paths can co-exist. An attempt, therefore, has been made in this laboratory to carry out oxidation-decomposition of the heptahydrate under controlled conditions and the results obtained from this study would be discussed in Part II of the communication.

Experimental

Methods of preparation

During our detailed studies on the thermal analysis of ferrous sulphate heptahydrate, we have prepared this compound as also other hydrates and oxidation products as intermediates. General methods of preparation of these compounds and their analyses are described here.

Ferrous sulphate heptahydrate, $FeSO_4 \cdot 7\,H_2O$

Analytical reagent grade ferrous sulphate heptahydrate was dissolved in hot $2N$ sulphuric acid to make a saturated solution and filtered. To the filtrate, absolute alcohol (about half the volume of the filtrate) was added with stirring and the mixture was allowed to cool. The crystallized hydrated ferrous sulphate was filtered and washed with absolute alcohol several times. The crystals were dried by pressing between the folds of a filter paper. Further drying was done by passing a stream of pure carbon dioxide over the sample. The sample thus prepared is stable for more than 30 days.

Ferrous sulphate tetrahydrate, $FeSO_4 \cdot 4\,H_2O$

This compound was prepared from the heptahydrate obtained above by keeping it under reduced pressure in a vacuum desiccator over fused calcium chloride for about 26 hours. It was preserved in a desiccator over fused calcium chloride.

Ferrous sulphate monohydrate, $FeSO_4 \cdot H_2O$

The monohydrate was prepared by the following method [33]: To 50 ml of warm 50% (*V*/*V*) sulphuric acid, 100 g of the heptahydrate were added with stirring. The mixture was kept on a water bath for one hour with frequent stirring. The white powder formed was transferred on to a sintered glass funnel (porosity zero) and washed several times successively with absolute alcohol and dry ether. It was then pressed between the folds of a filter paper and preserved in a stoppered bottle over fused calcium chloride.

Hydroxy sulphate, $Fe(OH)SO_4$

Powdered ferrous sulphate heptahydrate (−60 mesh) was placed in a petri dish and heated at 250−300° for a period of about 24 hours. The light yellow powder of hydroxy iron sulphate was preserved in a stoppered bottle over fused calcium chloride.

Oxo iron sulphate, $Fe_2O(SO_4)_2$

Powdered ferrous sulphate heptahydrate (−60 mesh) was placed in a flat platinum dish and heated at 415 ± 10° for a period of about 20 hours. The brownish red powder of oxo iron sulphate was preserved in a stoppered bottle over fused calcium chloride.

Analysis

The various compounds described above were analyzed for free acid, ferrous iron, ferric iron, sulphate content and combined water. The following procedures were used.

Determination of free acid: About 1 g of the substance was weighed into a 100 ml volumetric flask and shaken thoroughly with 50 ml distilled water for a few seconds. After making up the volume the pH of the suspension was measured immediately. The free acid content was computed from the pH value.

Determination of ferrous and ferric iron: The material under investigation was dissolved in hydrochloric acid in an inert atmosphere. The ferrous and ferric contents were determined titrimetrically by the standard dichromate method.

Determination of sulphate and combined water (including free water if any)

Determination of water molecules in ferrous sulphates poses serious difficulties on account of the tendency of ferrous iron to undergo oxidation-decomposition. The estimation of sulphate by the barium sulphate method is time consuming and tedious. A simpler procedure was, therefore, considered necessary. It depends on the reaction of hydrates and basic salts with either anhydrous sodium carbonate or anhydrous magnesium oxide. The method is unique in as much as both sulphate and water molecules are analyzed in a single run.

By reaction with anhydrous sodium carbonate:

The reactions of ferrous sulphate and basic salts with anhydrous sodium carbonate may be represented by:

$$2\,FeSO_4 \cdot xH_2O + 2\,Na_2CO_3 + 1/2\,O_2 = 2\,Na_2SO_4 + Fe_2O_3 + 2\,CO_2 + 2xH_2O \tag{10}$$

$$2\,Fe(OH)SO_4 + 2\,Na_2CO_3 = 2\,Na_2SO_4 + Fe_2O_3 + 2\,CO_2 + H_2O \tag{11}$$

$$Fe_2O(SO_4)_2 + 2\,Na_2CO_3 = 2\,Na_2SO_4 + Fe_2O_3 + 2\,CO_2 \tag{12}$$

One gram of the material under investigation was mixed with one gram of anhydrous sodium carbonate and ground together in an agate mortar. The mixture was transferred into a tared platinum dish and heated at $500 \pm 10°$ for 1 hour or till constant weight is obtained. The difference in weight (w) corresponds to (a) weight loss due to water, (b) weight loss due to carbon dioxide and (c) weight gain due to oxidation (where ferrous iron is present). The mass after weighing is extracted with distilled water and filtered. The residue is washed a few times with distilled water. The filtrate and washings were collected in a standard volumetric flask and made up to the mark. The unreacted sodium carbonate in this solution was analyzed acidimetrically. From this value, the reacted carbonate (w_1) and the loss due to carbon dioxide(x) were calculated. The weight gain due to oxidation(y) was obtained by determining the ferrous content and by using Eq. (10). The weight loss due to water was computed from these values and corresponds to $w - x + y$. In case of hydroxy iron sulphate the reaction with sodium carbonate gives only loss due to the expulsion of water and carbon dioxide (Eq. 11). The difference in the total loss (w) and the loss due to carbon dioxide (x) gives the content of water present in the material. The reaction of oxo iron sulphate with sodium carbonate results only in the evolution of carbon dioxide (Eq. 12). In all the three cases the sulphate content was determined from the amount of sodium carbonate reacted (w_1) according to Eqs 10, 11 and 12.

By reaction with anhydrous magnesium oxide:

The reactions of hydrates of ferrous sulphate and basic salts with anhydrous magnesium oxide may be represented by:

$$2\,FeSO_4 \cdot xH_2O + 2\,MgO + 1/2\,O_2 = 2\,MgSO_4 + Fe_2O_3 + 2xH_2O \qquad (13)$$

$$2\,Fe(OH)SO_4 + 2\,MgO = 2\,MgSO_4 + Fe_2O_3 + H_2O \qquad (14)$$

$$Fe_2O(SO_4)_2 + 2\,MgO = 2\,MgSO_4 + Fe_2O_3 \qquad (13)$$

The procedure here is the same as described under the sodium carbonate method. The difference (w) corresponds to weight loss due to water and weight gain due to oxidation (where ferrous iron is present). In the filtrate, magnesium (w_1) was determined complexometrically. In the case of basic salts (Eq. 14) where no oxidation takes place the value w gives directly the amount of water in the compound. Where oxidation occurs (Eq. 13), the weight gain due to oxidation (y) was obtained determining the ferrous content and by using Eq. 13. The weight loss due to water is then given by $w + y$. In all the three cases the sulphate content is determined from the amount of $MgSO_4$ (w_1) formed according to Eqs 13, 14 and 15.

Data presented in Table 2 for ferrous sulphate heptahydrate show that both sodium carbonate and magnesium oxide methods give good results for sulphate content. Some correction for sulphate content is to be made in both cases if free acid is more (say greater than 1 %) as both sodium carbonate and magnesium oxide react with free acid and thus give higher values for magnesium oxide method and lower values for sodium carbonate method. The correction can, however, be made easily from the known free acid content. The method utilising the reaction with sodium carbonate gives slightly higher values for water owing to some decomposition of sodium carbonate. However, the magnesium oxide method does not suffer from this draw back. Thus magnesium oxide method is preferred and will be followed throughout this investigation.

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Résumé — On présente une mise au point bibliographique sur les publications concernant l'analyse thermique dans l'air du sulfate de fer(II) heptahydraté. La décomposition oxydante du sulfate de fer(II) heptahydraté est une fonction complexe des conditions expérimentales. On expose et discute quelques méthodes générales, y compris celles que les auteurs ont développées, afin d'analyser les différents états intermédiaires intervenant lors de la décomposition oxydante de l'heptahydrate.

Zusammenfassung — Eine Literaturübersicht über die Thermoanalyse der Eisen(II)sulfat Heptahydrate in Luft wird gegeben. Die oxidative Zersetzung des Eisen(II)sulfat Heptahydrats ist eine komplexe Funktion der Versuchsbedingungen. Einige allgemeine Methoden, einschließlich der von den Autoren zur Analyse verschiedener im Laufe der oxidativen Zersetzung des Heptahydrats entstehenden Zwischenverbindungen, werden beschrieben und erörtert.

Резюме — Представлено обозрение литературы по термоанализу гептагидрата сульфата железа(II). Окисление-разложение гептагидрата сульфата железа(II) сложным образом зависит от экспериментальных условий. Представлены и обсуждены общие методы, включая и разработанные авторами для анализа различных промежуточных продуктов, встречающихся во время окисления-разложения гептагидрата.