MÖSSBAUER STUDIES OF THE THERMAL DECOMPOSITION OF IRON(II) AMMONIUM SULPHATE HEXAHYDRATE

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The thermal decomposition products of Mohr's salt, $(NH_4)_2Fe(SO_4)_2.6 H_2O$, in static air have been studied in the temperature range 25—800°. Mössbauer spectroscopy, X-ray diffractometry and thermal analysis were used in the identification of the intermediates. Fe^{2+} compounds containing 4, 2 and zero H_2O were identified and the possibility of occurrence of $(NH_4)_2Fe_2(SO_4)_3$ is advanced. The presence of Fe^{3+} was detected starting at 230° for a 1.6°/min heating rate, and the compounds $(NH_4)Fe(SO_4)_2$ and $Fe_2(SO_4)_3$ were also identified.

Mohr's salt, iron(II) ammonium sulphate hexahydrate, $(NH_4)_2Fe(SO_4)_2.6 H_2O$ (hereafter HHFAS), belongs to the monoclinic crystal system, space group $P 2_{1/a}$, with unit-cell dimensions $a = 9.32$ Å, $b = 12.65$ Å and $c = 6.24$ Å and $\beta = 106.8°$ [1]. Its thermal decomposition products have been studied by several authors [2—4]. The results were vague and not absolutely conclusive. Whereas Pascal indicates a loss of water and some ammonia from 100° onwards, and the formation at 290° of the anhydrous alum $(NH_4)Fe(SO_4)_2$, Wendlandt indicates the range from 192 to 310° extending up to 450°.

The present work describes the identification of the thermal decomposition products of HHFAS under non-isothermal conditions and combines the capabilities of thermal analysis [5] and Mössbauer spectroscopy [6].

As only small changes were to be expected between some of the decomposition products of HHFAS, it was felt that Mössbauer spectroscopy, with its unique capability of detecting small variations in the coordination sphere of iron atoms, was extremely suitable for this purpose.

The aim of the present study is to give as detailed as possible an account of the development of the thermal decomposition of HHFAS and to determine the temperature of passage from Fe^{2+} to Fe^{3+}. No gas analysis was performed and X-ray identification at room temperature was performed only for the less hygroscopic products.

Experimental

The samples used were Merck reagent grade (natural unenriched iron) HHFAS and were heated in static air in a derivatograph manufactured by MOM (Budapest), model 1969. This equipment gives simultaneously the mass loss curve (TG),

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the derivative of the mass loss (DTG) and the DTA curve. It also gives the temperature (T) inside the sample. The heating system can be stopped at any temperature of interest, due to the fact that all four curves can be followed simultaneously by visual inspection. By this procedure the beginning, the maximum rate and the end of the a chemical reaction due to the heating process can be determined, and a quenching method can be attempted in order to isolate different compounds or phases. The minima of the DTA curve [7] and some intermediate points were used in the present study to prepare the products of thermal decomposition of HHFAS, by quenching each one to room temperature. Several heating rates were tried in order to study all the details of the thermal decomposition process without loss of information: 1.6°/min was chosen. Each sample (1 g HHFAS) was heated to the desired temperature, and removed from the oven to a glove-bag filled with commercial Ar, where the encapsulation was performed. Typical times required to transfer the samples from the oven to the bag, and to encapsulate them, were 5 and 15 min, respectively. "O" ring sealed absorber holders were used, with an effective area of 2.5 cm². Mössbauer spectra were run with around 30 to 40% of the total sample after mixing the several layers of different shapes and compactness which could be detected in the crucible taken from the oven. This led to somewhat thick Mössbauer samples (up to a maximum total iron content of 25 mg/cm²). Tightness of the absorber holders was checked by running the spectra of several samples over a period of 3 weeks, with no appreciable change of the relative intensity of the components of the mixture, whereas opening of the absorber holders for a few minutes (and subsequent reclosing) introduced a noticeable change. Therefore, any possible rehydration of the samples must have occurred in the period of the quenching process and sample encapsulation in a water-poor atmosphere.

A constant acceleration Mössbauer effect spectrometer built around a PDP 11/10 computer, together with a NaI(Tl) scintillation counter and a conventional amplifying line, were used. The software was programmed so as to obtain a triangular velocity wave form and the accumulation was performed on separate halves (256 channels each) of the computer memory for the increasing and the decreasing velocities, respectively. Deviations from linearity are less than 0.5% over some 95% of the wave form. Deviations from reproducibility over a 45-day period are better than 1%, as shown with frequent calibrations with sodium nitroprusside (SNP), which is also used as reference material for the isomer shifts (IS). A room-temperature ^{57}Co in Rh source, of approximately 15 mCi strength, purchased from NENC, was used.

A standard least squares fitting procedure, using independent lorentzian lines, was performed on each half of the spectra. The reported values are the means of the values for the two halves, which never differed by more than the above mentioned linearity limit.

The more complex spectra (230° and 260°) were analyzed using a stripping method which we have previously reported [8]. Both methods were used on a HP-2100 A computer with a 16K bite memory.

For the original HHFAS we always found a slight difference between the areas of the two peaks, that for the lower velocity peak being around 10% larger.

The statistics of the spectra up to 142° were of the order of $5 \cdot 10^5$ points/channel. The higher-temperature samples were run up to $8 \cdot 10^5$ points/channel, which means a statistical error (0.11%) at least 5 times lower than the weakest experimental peak.

Discussion and interpretation of results

Table 1, 2 and 3 summarize the room-temperature Mössbauer effect results for the different samples, labelled with the interruption temperature for the thermal treatment. Typical spectra are shown in Figs 1 and 2. The thermal curves are
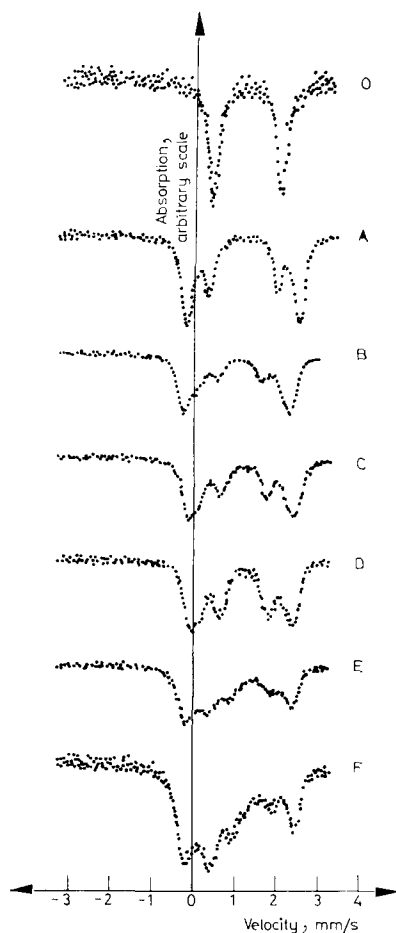

Fig. 1. Room-temperature Mössbauer spectra of the products obtained on heating $(NH_4)_2Fe(SO_4)_2.6 H_2O$ in static air at a rate of 1.6°/min, up to a temperature of 0 = room; $A = 118°$; $B = 142°$; $C = 160°$; $D = 165°$; $E = 230°$; $F = 260°$

Table 1

Mössbauer parameters of the compounds $Fe(NH_4)_2(SO_4)_2 \cdot nH_2O$ obtained on heating ferrous
ammonium sulphate hexahydrate (Mohr's salt) up to 165° at a rate of 1.6°/min. Errors on the
last figures quoted in brackets

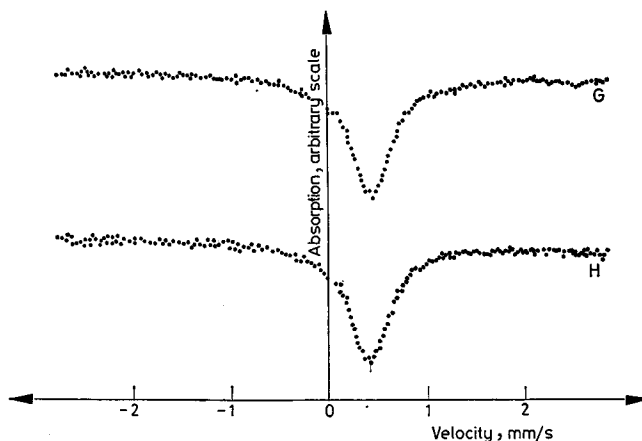| Sample heated up to	Peaks numbers	IS*, mm/s		QS, mm/s		Relative intensities	n
Original HHFAS		1.50	(2)	1.72	(2)	1	6
118°	1—4	1.52	(4)	2.70	(8)	0.66	6
	2—3	1.50	(4)	1.73	(8)	0.34	4
142°	1—8	1.49	(6)	2.75	(12)	0.35	4
	2—7	1.48	(6)	2.38	(12)	0.35	2
	3—6	1.45	(6)	1.73	(12)	0.12	6
	4—5	1.51	(6)	1.11	(12)	0.18	0
160°	1—6	1.53	(5)	2.70	(10)	0.33	4
	2—5	1.53	(5)	2.29	(10)	0.35	2
	3—4	1.54	(5)	1.16	(10)	0.32	0
165°	1—6	1.50	(5)	2.60	(10)	0.21	4
	2—5	1.49	(5)	2.19	(10)	0.41	2
	3—4	1.51	(5)	1.16	(10)	0.38	0

* Referred to standard SNP.

Fig. 2. Room-temperature Mössbauer spectra of the products obtained on heating
$(NH_4)_2Fe(SO_4)_2 \cdot 6\ H_2O$ in static air at a rate of 1.6°/min (oxidative region) up to a temperature
of: $G = 370°$; $H = 450°$

Table 2

"Stripping" of Mössbauer spectra of the decomposition products of HHFAS heated up to temperature T at a rate of 1.6°/min. Typical uncertainties for the procedure are 0.1−0.15 for QS and 0.05−0.08 for IS

Heating temperature, T	Compound	IS*, mm/s	QS, mm/s	Fraction
230°	$(NH_4)_2Fe(SO_4)_2 \cdot 4 H_2O$	1.4	2.6	0.32
	$.2 H_2O$	1.4	2.2	0.22
	$.0 H_2O$	1.5	1.1	0.19
	Fe(III) compound	0.7		0.27
			Total	1.00
260°	$(NH_4)_2Fe(SO_4)_2 \cdot 4 H_2O$	1.6	2.6	0.32
	$.2 H_2O$	1.4	2.3	0.17
	$(NH_4)_2Fe_2(SO_4)_3$	1.5	0.7	0.15
	Fe(III) compound	0.7		0.39
			Total	1.03

* Referred to standard SNP

Table 3

Mössbauer parameters of the decomposition products of $(NH_4)_2Fe(SO_4)_2 \cdot 6 H_2O$ heated in static air at a rate of 1.6°/min up to a temperature T (Fe^{3+} region)

$T, °$	IS*, mm/s	Main compound (identified through X-rays)
370	0.73 ± 0.04	$(NH_4)Fe(SO_4)_2$
450	0.73 ± 0.04	$Fe_2(SO_4)_3$

* Referred to standard SNP. To convert to a $^{57}Co/Pd$ source as used in ref. 3, subtract typically 0.44 mm/s.

shown in Fig. 3 up to 450°. Spectrum 0 of Fig. 1 corresponds to the original hexa-hydrated compound as taken from the shelf. Typical linewidths are 0.29 mm/s, and both hyperfine parameters, IS and QS, are in good agreement with published data [9−13].

After thermal treatment up to 118°, spectrum A of Fig. 1 is obtained. This spectrum has been properly fitted with four peaks; the 2 inner ones (see Table 1) re-

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produce accurately the HHFAS hyperfine parameters, and show similar width
and intensity ratios as the pure salt. The two other peaks lead to an IS of $1.52\pm$
±0.03 mm/s and a QS of 2.7 ± 0.08 mm/s. The possibility of these two peaks being
due to $FeSO_4$ or any of the dehydration products of $FeSO_4.7 H_2O$ [14, 15] due
to the loss of ammonia is dismissed, as studies of the rehydration kinetics of sample
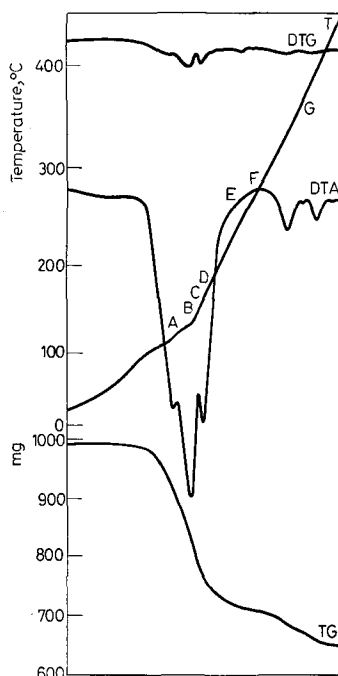A [17] reveal that the sample, when open to the air, reverts quantitatively to

Fig. 3. Thermal analysis curves for the decomposition in static air of 1000 mg
$(NH_4)_2Fe(SO_4)_2.6 H_2O$ at a rate of $1.6°/min$

HHFAS after appropriate periods of time. The loss of two molecules of water,
which would stoichiometrically lead to a 9.2% mass decrease, is in good agree-
ment with the value of 915 mg found from the TG curve (8% difference) at this
temperature. Point A corresponds to the beginning of a small flat region in the
DTG curve and a relative minimum in the DTA one. The next spectrum (Fig. 1B)
was taken with the 142° (B) sample. Point B corresponds to the minima of the
DTA and DTG curves. It shows a reduced quantity of the original HHFAS peaks
(12%) plus an overlap of 6 other peaks. The two outer ones can be joined in a pair
which reproduces the parameters of the tetrahydrate (THFAS) found in the pre-
vious spectrum. The relative area corresponding to THFAS drops from 0.66 to
0.35. On account of their similar intensities, we pair peaks 2 and 7, and 4 and 5
together. The subsequent spectrum (Fig. 1C) corresponds to the 160° (C) sample

taken ideally at the point of highest reaction rate of the DTA curve, which corresponds also to one in the DTG curve. As a matter of fact it was taken somewhat later, as it is impossible to detect the relative maximum without passing it. It required the use of only 6 peaks to fit the data properly. As the original HHFAS disappears, the IS and QS data are the same for the 3 remaining pairs as in the former spectrum, within the experimental uncertainties.

The 165° (D) spectrum (Fig. 1D) again shows the same characteristics. Point D is a relative minimum in both DTG and DTA curves. The only difference lies in the relative ratio of the 3 different Mössbauer patterns, which changes with increasing quenching temperature (for the pairs of peaks ordered with decreasing QS) from 0.35 : 0.35 : 0.18 to 0.33 : 0.35 : 0.32, and then 0.28 : 0.34 : 0.38.

The fact that the proportion for the THFAS decreases with increasing quenching temperatures and for the third pair increases for the same sequence may suggest, under the hypothesis of no (or very little) rehydration, that the peaks which correspond to the "second" pair of peaks (peaks 2 and 5) belong to the dihydrate, DHFAS, and the "third" (peaks 3 and 4) to the anhydrous product, AFAS. It is noteworthy that the IS for all of them lies around 1.50 mm/s (relative to SNP), whereas the quadrupole interaction varies considerably. This is in agreement with data reported in the literature for other compounds with several hydrate stages, $FeSO_4$ and $FeCl_2$ among others [6], where it has been found that the passage from one to another hydrate produces small changes in IS and considerable larger ones in QS.

The hypothesis of 4 hydrate steps (with 6, 4, 2 and 0 molecules of water) is compatible with the fact that the crystal structure shows that there are three different $Fe-H_2O$ distances in the crystal lattice [1], 2.156, 2.136 and 2.086 Å, and the overlapping of their spectra corresponds with the fact that the TG curve does not show a horizontal region for any of them.

Rehydration experiments in air with the 160° sample reinforce the previous arguments, as (after appropriate long periods) they reproduce nearly only HHFAS. Therefore, all the involved products seem to be related to HHFAS only by hydration processes [17].

The mass loss corresponding to the reaction

$$(NH_4)_2Fe(SO_4)_2.4\ H_2O \leftrightarrows (NH_4)_2Fe(SO_4)_2 2\ H_2O + 2\ H_2O$$

is in good agreement with the mass determined by TG at 142° (816.3 theoretical, 820 experimental).

The fact that at 142° we find not only DHFAS but another compound, which we suspect to be AFAS, could be explained as due to a low activation energy reaction which takes place in the sample, 2 DHFAS = AFAS + THFAS. The low thermal variation for the reaction agrees with the practically continuous TG curve, which only shows a very small kink for this temperature. Spectrum E was taken with the sample quenched from up to 230°, which corresponds to a point before the small kink on the DTA curve, whereas spectrum F corresponds to the temperature 260°. The two spectra could not be fitted properly by the customary

procedure, so we reverted to the "stripping" procedure, which is based on the fact that known spectra are subtracted from the experimental one, trying to avoid overshoots in the "difference" spectra and to arrive finally at a flat background line. This procedure is not univocal, as it depends on the order in which the spectra are subtracted and on the allowance which is made in the variation of their parameters. Several trials were made for each spectrum, allowing for these factors. Quality of fits is tested through a X^2 criterium, and the variation of the parameters is performed using this test and visual inspection of the generated, the difference and the addition spectra. Table 2 shows the results for the stripping of the 230 and 260° spectra. We consider them as very good, as they explain the area of the spectra within 1 and 3% without noticeable overshoots which may mask the significance of these data.

Two facts are immediately noticeable: i) the appearance of an Fe(III) compound, and ii) the disappearance of $(NH_4)_2Fe(SO_4)_2$ and the appearance of another doublet, with parameters IS = 1.5 mm/s (vs. SNP) and QS = 0.7 mm/s, which may be due to $(NH_4)_2Fe_2(SO_4)_3$. This transformation may correspond to the small peak in the DTA curve, which has only a very subtle corresponding peak in the DTG curve. This is a plausible explanation, as under the present circumstances the reaction

$$2(NH_4)_2Fe(SO_4)_2 \leftrightarrows (NH_4)_2Fe_2(SO_4)_3 + (NH_4)_2SO_4$$
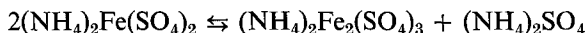
may maintain the ammonium sulphate trapped, and retain the decomposition products above the normal decomposition temperature (160°). Whereas this point and the identification of the compound which appears at 260° may be a matter of controversy, it is quite clear that the oxidation process begins below 230° and is responsible for the slope in the TG curve. These facts are also supported by the rehydration studies on the 230 and 260° samples, which will be published elsewhere, which show that an Fe^{3+} peak (IS = 0.70 mm/s vs. SNP) remains, whereas the rest is converted back to HHFAS.

Spectra G and H (Fig. 2) are those of the 370 and 450° samples. Both correspond to Fe^{3+} species, with practically no traces of Fe^{2+} (certainly less than 1%). Due to the nature of the electronic structure of this ion, which corresponds to a half-filled 3d shell, these ions usually show no (or a very small) quadrupole splitting, and their Mössbauer spectra are therefore not very sensitive to the detailed nature of the compounds. Hence, we are not able to decide between $(NH_4)Fe(SO_4)_2$, $(NH_4)_3Fe(SO_4)_3$ and $Fe_2(SO_4)_3$ or another conceivable species. From the X-ray diffractograms it is clear that the 370° sample contains mainly $(NH_4)Fe(SO_4)_2$, and the 450° sample $Fe_2(SO_4)_3$, in agreement with Heilmann et al. [3], whose studies were performed isothermally. This transformation explains, therefore, the peak at 390° in the DTA curve. The peak at 335° for the same curve probably corresponds to the main oxidative step which converts $(NH_4)_2Fe_2(SO_4)_3$ into $(NH_4)Fe(SO_4)_2$ through an undetermined pathway.

Finally, between 450° and 760° only $Fe_2(SO_4)_3$ was detected by X-ray analysis, and above 760° only α-Fe_2O_3 is present, which is a very well known transformation.

Conclusions

In the present work we have determined several steps in the thermal decomposition of HHFAS and found the Mössbauer parameters for dehydration products. At least 3 iron(II) compounds were identified, with 4, 2 and 0 water molecules, and a fourth one, possibly $(NH_4)_2Fe_2(SO_4)_3$, appears at around 230°. Simultaneously we determined the presence of trivalent iron at 230°, well below the previously accepted temperature. The exact nature of the compound could not be determined, due to the intrinsic electronic properties of the trivalent iron atom, which are reflected in a certain poorness of features in the Mössbauer spectra. The details of the thermal curves are satisfactorily accounted for, especially up to 260°, where the Fe(III) compounds start to be of primary importance.

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RÉSUMÉ — On a étudié, dans l'intervalle de températures compris entre 25° et 800°, les produits de la décomposition thermique du sel de Mohr $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ dans l'air statique. Afin d'identifier les composés intermédiaires, on s'est servi de la spectroscopie Mössbauer, de la diffractométrie aux rayons X et de l'analyse thermique. On a identifié des composés Fe^{+2} à 4, 2 et zéro H_2O et avancé la possibilité de la présence de $(NH_4)_2Fe_2(SO_4)_6$. On a décelé la présence de Fe^{+3} à partir de 230° avec une vitesse de chauffage de 1.6°/min et on a identifié également les composés $(NH_4)Fe(SO_4)_2$ et $(Fe_2(SO_4)_6$.

ZUSAMMENFASSUNG — Die thermischen Zersetzungsprodukte des Mohr'schen Salzes $(NH_4)_2$ $Fe(SO_4)_2 \cdot 6H_2O$ in statischer Luft wurden im Temperaturbereich von 25° bis 800° untersucht. Mössbauer-Spektroskopie, Röntgendiffraktometrie und Thermoanalyse wurden zur Identifizierung der Zwischenprodukte eingesetzt. Fe^{+2}-Verbindungen mit 4, 2 und 0 H_2O wurden nachgewiesen und die Möglichkeit des Vorkommens von $(NH_4)_2Fe_2(SO_4)_6$ erwähnt. Das Vorligen von Fe^{+3} wurde von 230° beginnend bei 1.6°/min Aufheizgeschwindigkeit nachgewiesen. Die Verbindungen $(NH_4)Fe(SO_4)_2$ und $Fe_2(SO_4)_6$ wurden ebenfalls identifiziert.

Резюме — Изучено термическое разложение соли Мора $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ в статической атмосфере воздуха в температурной области 25—800°. Для идентификации промежуточных соединений были использованы мёссбауэровская спектроскопия, рентгенодифрактометрия и термический анализ. Были идентифицированы соединения Fe^{2+}, содержащие 4 молекулы воды, 2 молекулы или же безводные. Показана вероятность местонахождения молекул воды. Присутствие Fe^{3+} было обнаружено, начиная от 230° при скорости нагрева 1.6°/мин. и были идентифицированы соединения $(NH_4)Fe(SO_4)_2$ и $Fe_2(SO_4)_3$.