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THE DECOMPOSITION OF IRON(III) SULFATE IN AIR

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The decomposition of initially hydrated powders of iron(III) sulfate was carried out in air over the temperature range 823–923 K. The decomposition process, which gave Fe_2O_3 as a solid product, was seen to have zero-order kinetics and an activation energy of 219 $kJ\cdot mol^{-1}$. The nature of the product and the kinetics of decomposition were the same for samples decomposed in air and in argon. Sulfate samples with additives of FeS and Fe_2O_3 were also decomposed under similar conditions and the results confirmed the zero-order kinetics (for the case of the Fe_2O_3 additives) and the lack of effect of FeS on the decomposition of iron(III) sulfate.

Aside from contributing to the understanding of dissociation reactions, studies on the decomposition of metal sulfates have been the focus of attention for practical applications. Among such applications is the proposed use of decomposition reactions in the generation of hydrogen [1, 2]. Our current interest in the decomposition of iron(III) sulfate is a consequence of an investigation on the oxidation of iron sulfide [3]. The oxidation of the sulfide is reported to involve the formation of iron(III) sulfate as an intermediate phase [4]. The decomposition of iron(III) sulfate is reported to proceed through the reaction [5, 6]

$$Fe_2(SO_4)_3 = Fe_2O_3+3SO_3 \qquad (1)$$

which can be followed by

$$2SO_3 = 2SO_2+O_2 \qquad (2)$$

In this paper we report on the decomposition of initially hydrated iron(III) sulfate in an atmosphere of dry air.

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Experimental

Hydrated iron(III) sulfate powders, $Fe_2(SO_4)_3 \cdot xH_2O$, with a reported purity of 99.8% were obtained from Mallinckrodt. The dehydration and subsequent decomposition of this material were accomplished in a Cahn continuous recording microbalance (Model 1000) which had an accuracy of 18 µg. Details of the apparatus utilized in this study have been reported in previous publications [7, 8].

In each experiment 100.00 mg of the hydrated sulfate was placed in an alumina crucible and loaded into the reaction tube. The entire apparatus was evacuated to a pressure less than 27 mPa (2×10^{-4} torr) and was then back-filled to one atmosphere with argon gas. It was subsequently reevacuated and back-filled with room air which had passed through both a drier and a molecular sieve before entering the system. The room air port was then closed and a flow of air was established. The flow was established through the use of commercially-purchased compressed air which was also passed through a drier and a molecular sieve prior to entering the reaction tube. A flow rate of approximately 430 ml $\cdot$ min^{-1} was sustained throughout the experiment in order to avoid the depletion of oxygen at the sulfate/oxygen interface. The air stream entered the reaction tube through the bottom and exited out through a side tube and a bubbler attached to the top of the reaction tube.

Samples were heated at a constant rate of 10 deg min^{-1}, and the temperature was measured by means of a Pt/Pt–10%Rh thermocouple placed in the vicinity of the sample crucible in the constant temperature region of the surrounding tube furnace. Decomposition of iron(III) sulfate was carried out over the temperature range 823–923 K.

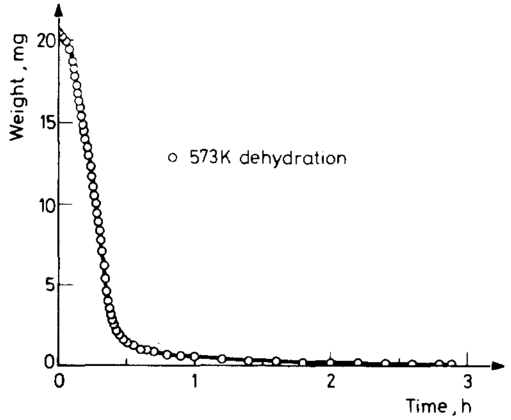

Fig. 1 Dehydration of iron(III) sulfate at 573 K

As stated above, the sulfate used in the experiments was a hydrated salt, and thus it had to be dehydrated prior to decomposition. Preliminary dehydration experiments were carried out in a vacuum of $p < 6.7$ mPa (5×10^{-5} torr) at 473 and 533 K, and it was determined that a temperature of at least 573 K was required to ensure complete dehydration. The results of a typical iron(III) sulfate dehydration experiment at 573 K are shown in Fig. 1. This figure shows that over 20 mg of the 100.00 mg hydrated sulfate samples was lost during dehydration, indicating that $x = 11.6$. After dehydration, $Fe_2(SO_4)_3$ samples were decomposed in flowing air at 823, 860 and 923 K. In addition to the air decompositions, one decomposition experiment was carried out in a flow of argon gas at 860 K. This experiment was performed in order to determine whether oxygen played a role in the decomposition process. Experiments were also carried out wherein the sulfate was mixed with either FeS or Fe_2O_3.

Results and discussion

Because the addition of other materials to the $Fe_2(SO_4)_3$ required removing the sample from the dry reaction tube for approximately 35 minutes, control samples of $Fe_2(SO_4)_3$ were also removed from the reaction tube following dehydration for an equivalent period of time before being decomposed in flowing air. Iron(III) sulfate, like most similar salts, is very hygroscopic. The 35 minute exposure to room air conditions caused the material to adsorb water. Exposure to the high temperature of the subsequent decompositions caused the water to be re-released. This effect is noticeable in the initial portions of some decomposition curves. Figure 2 shows the results of two 860 K decompositions. In one case, the sample was removed from the tube and replaced after 35 minutes. In the other case, it was decomposed following dehydration without exposure to room air. The shape of decomposition portion of the curve is not altered, but the removal of the absorbed water is evident in the initial weight loss, approximately 2 mg of one of the samples. Because the dehydration occurs at a lower temperature than the decomposition, and hence at an earlier time (because of the constant heating rate up to temperature), the loss in water causes an effective time shift in the decomposition curve. The shape of the curve from 46 mg down to zero remains unchanged, however, as seen in Fig. 2.

Iron(III) sulfate decomposed at a constant rate throughout all but the last portions of the experiments. The rate of decomposition was, of course, temperature dependent. The results of three different sulfate decompositions are shown in Fig. 3. The results in this figure are all from samples which were exposed to air before decomposition. The 923 K sample was (incompletely) dehydrated at 473 K and hence contained more water initially than the other two samples, and the 823 K

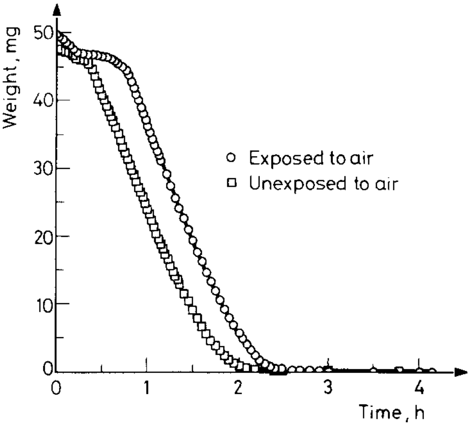

Fig. 2 The effect of prior room air exposure on the decomposition of iron(III) sulfate at 860 K

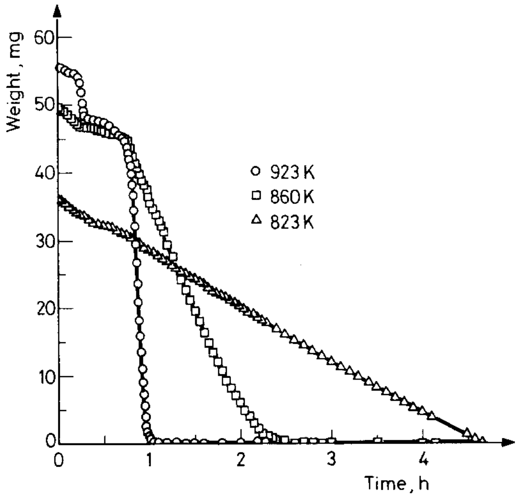

Fig. 3 The decomposition of iron(III) sulfate in flowing air. $T = 823$, 860 and 923 K

experiment was stopped before completion. However, the graphs are adjusted to show the final weight equalling zero, thus the starting weight of this sample (823 K) does not match the other starting weights. As can be seen from Fig. 3 the decomposition kinetics of $Fe_2(SO_4)_3$ appear to be linear or zero order, therefore, they can be described by

$$\Delta w = k \cdot t \tag{3}$$

where Δw is the weight loss in mg, t is time in hr, and k is the rate constant ($mg \cdot hr^{-1}$). Reaction rate constants were calculated from the constant slope regions of the curves of Fig. 3. The resulting rate constants are plotted in Fig. 4 and listed in Table 1. From the Arrhenius temperature dependence of the rate constant [$k = k_0 \exp(-E/RT)$], the activation energy, E, for decomposition can be evaluated. A least squares fit of the data gives a value of 219 $\mathrm{kJ \cdot mol^{-1}}$ for the activation energy associated with the decomposition of iron(III) sulfate in air.

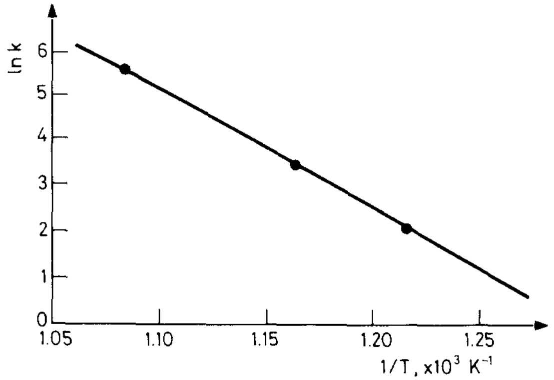

Fig. 4 The temperature dependence of the rate constant of the decomposition of iron(III) sulfate

Table 1 Rate constants for the decomposition of iron(III) sulfate

T, K	k, $\mathrm{mg \cdot hr^{-1}}$
823	8.4
860	31.6
923	265.0

To further investigate the kinetics of $Fe_2(SO_4)_3$ decomposition, experiments on iron(III) sulfate were performed in which other powders were added to the sulfate before decomposition. In some experiments, a small amount of FeS (approximately 15 mg) was added and the combination reacted in flowing air at 860 K. In other experiments, a large amount (200 mg) of reagent-grade Fe_2O_3 was added prior to the 860 K decomposition. In these experiments, as well as the normal sulfate experiments, there was approximately 80 mg of anhydrous iron(III) sulfate present before decomposition (refer to Fig. 1). In the sulfate-sulfide experiments, the resulting weight-time curves were, in effect, the summation of an FeS oxidation curve [3] and a $Fe_2(SO_4)_3$ decomposition curve (see Fig. 5). In other words, if the two powders had been reacted separately and the sample weights summed at various times, the resulting graph would be the same as Fig. 5. Nevertheless, the contribution of the FeS components was small compared to that of $Fe_2(SO_4)_3$. This was due to the fact that the amount of FeS added to the $Fe_2(SO_4)_3$ was small. In Fig. 5, the FeS component of the weight *vs.* time curve is identifiable by both the "peak" at approximately 1.0 hr and the non-zero slope around 3.0 hr (compare the 860 K data of Fig. 3 with those of Fig. 5). Besides the slight changes in the decomposition curve caused by the simultaneous oxidation of the FeS and decomposition of $Fe_2(SO_4)_3$, no change in the actual decomposition kinetics of the iron(III) sulfate is discernable (based on the steady-state rates of decomposition). The lack of interaction between the two materials is an important finding on the basis of observations on the decomposition of iron(II) sulfate [9]. It has been reported that the addition of either FeS or FeS_2 in the right amounts causes a marked increase in the decomposition rate of iron(II) sulfate, $FeSO_4$. According to the cited work, the interaction between FeS and $FeSO_4$ is reported to take place according to the following:

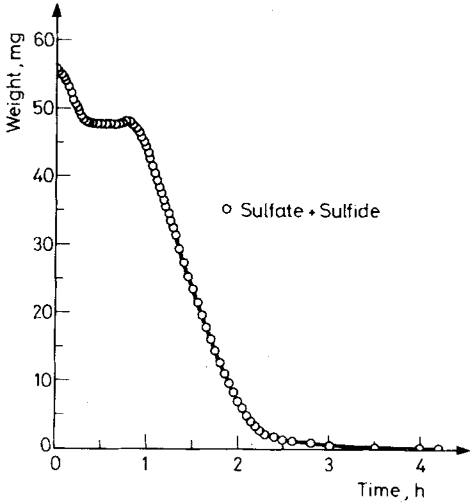

Fig. 5 The decomposition of iron(III) sulfate with FeS additive. T = 860 K

$$FeS + 7\,FeSO_4 \rightarrow 4\,Fe_2O_3 + 8\,SO_2 \qquad (4)$$

An equivalent expression for the coordinated reaction of FeS and $Fe_2(SO_4)_3$ would be:

$$6\,FeS + 7\,Fe_2(SO_4)_3 \rightarrow 10\,Fe_2O_3 + 27\,SO_2 \qquad (5)$$

Using Eq. (5), the weights of the two components corresponding to the molar relationship written above were calculated. The percentage (by weight) of FeS was found to be approximately 15%, and it was this fraction of FeS which was added to the anhydrous iron(III) sulfate before heating. The only product after almost five hours of heating at 860 K was Fe_2O_3. Although FeS and iron(II) sulfate are known to interact with an accompanying increased rate of sulfate decomposition, the same cannot be said for FeS and iron(III) sulfate on the basis of the present observations.

As stated earlier, Fe_2O_3 was also used as an additive in the iron(III) sulfate decompositions. The oxide powder was combined with the sulfate to form a homogeneous mixture which was then heated in the usual manner. The results showed the rate of sulfate decomposition to be the same with and without this additive. Specifically, the rate constants for sulfate plus oxide and sulfate alone are 32.7 and 31.6 $mg \cdot hr^{-1}$, respectively. Since Fe_2O_3 is the product of $Fe_2(SO_4)_3$ decomposition, it is interesting to note that the addition of large amounts of Fe_2O_3 caused no change in the kinetics, thus indicating that the reaction is irreversible and giving support to the conclusion that the decomposition is zero-order.

X-ray diffraction analyses were performed on the iron(III) sulfate samples. A sample of the dehydrated, as-received material showed no diffraction peaks at all. This is likely due to the gelatin-like structure of the hydrated sulfate. A dehydrated sample of iron(III) sulfate held in a dessicator until the time of X-ray analysis showed the material to be anhydrous iron(III) sulfate with a trace of $Fe_2(SO_4)_3 \cdot H_2O$. It is possible that the water was not removed during dehydration, but more likely, however, the water was resorbed during the X-ray analysis which was conducted in an ordinary room atmosphere. Sulfate samples whose decomposition was taken to completion in either air or argon gas gave only Fe_2O_3 as a product.

The water in the hydrated, as-received iron(III) sulfate material seemed to be attached to the sulfate more on a macroscopic rather than a microscopic scale. Figure 6(a) shows how the spherical sulfate particles seem to be trapped within the gelatin-like structure of the water. The sample in this SEM micrograph appeared to be made up of one large interconnected globule. After the water had been removed by dehydration, the sulfate particles were seen to resemble egg shells, thin and spherical (see Fig. 6(b)). The individual particles generally were nearly complete. A sample of fully decomposed iron(III) sulfate was also examined under the SEM, Fig. 6(c). This material, which had transformed into Fe_2O_3, showed signs of its original structure, although the average particle size was much smaller. Based on the micrographs shown in Fig. 6, the unreacted sulfate "spheres" were approximately 30 to 100 μm in diameter. After decomposition, however, the resulting Fe_2O_3 pieces were as small as 3 μm. Comparing Fig. 6(b) to Fig. 6(c), it is not surprising that the specific surface area of the sulfate increased from 0.58 to 48.0 $m^2 \cdot g^{-1}$ during decomposition.

The exact nature of the hydrated iron(III) sulfate was not specified by the supplier

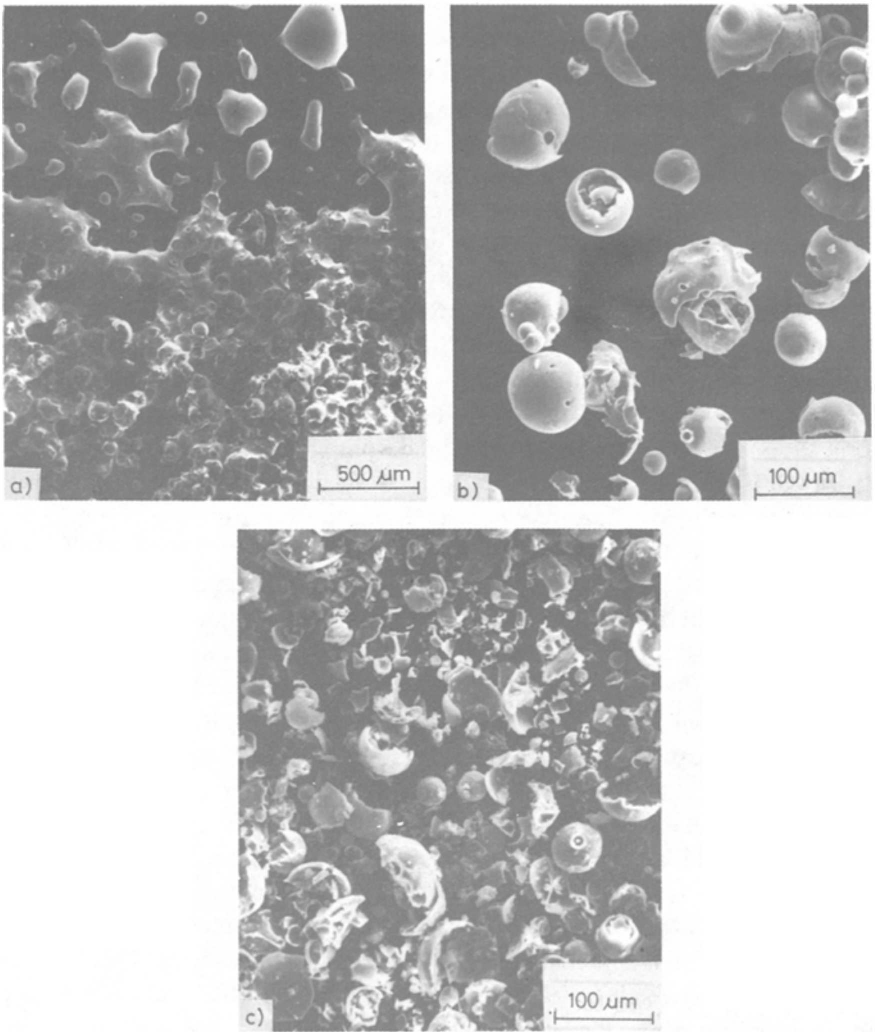

Fig. 6 (a) Scanning electron micrograph of hydrated iron(III) sulfate; (b) SEM of unhydrated iron(III) sulfate; (c) SEM of fully decomposed iron(III) sulfate

in terms of the number of water molecules per mole of $Fe_2(SO_4)_3$. Calculations based on the weight loss during the 573 K dehydrations (Fig. 1) implied an average of 11.6 moles of attached water. The amount of water removed during the dehydration of the material was found to depend on the dehydration temperature. Dehydrations in vacuum at 473 and 533 K did not remove as much water as dehydrations at 573 K. Some of the water lost during dehydration was resorbed into the samples when they were removed from the reaction tube for 35 minutes. This added water did not seem to affect the decomposition kinetics, however, since the water was removed again before the start of sulfate decomposition, see Fig. 2.

The kinetics of the decomposition of iron(III) sulfate appear to obey zero-order dependence with an activation energy of 219 $kJ \cdot mol^{-1}$. Other investigators have examined the decomposition of $Fe_2(SO_4)_3$ with no apparent agreement on either the kinetic order or the magnitude of the activation energy for the process. For example, Warner and Ingraham [5] decomposed iron(III) sulfate in nitrogen in the temperature range 973–1123 K and concluded that the kinetics are zero-order and the activation energy is 83.3 $kJ \cdot mol^{-1}$. In contrast, Pechkovskii et al. [10] decomposed $Fe_2(SO_4)_3$ in air over roughly the same temperature range (953–1003 K) but obtained much different results. They concluded that the kinetics of decomposition can be best described by a modified cubic relation and that the activation energy for the decomposition process was 289.3 $kJ \cdot mol^{-1}$.

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REFERENCES

1 G. E. Besenbruch, K. H. McCorkle, J. H. Norman, D. R. O'Keefe, J. R. Schster and M. Yoshimoto, Proc. Third World Hydrogen Conf., Tokyo, Pergamon Press, Oxford 1980, p. 243.
2 P. W. T. Lu and R. L. Ammons, Proc. Third World Hydrogen Conf., Tokyo, Pergamon Press, Oxford 1980, p. 439.
3 P. G. Coombs and Z. A. Munir, submitted to Metall. Trans., 1988.
4 H. J. Shyu, P. P. Vaishnava and P. A. Montano, Fuel, 60 (1981) 1023.
5 N. A. Warner and T. R. Ingraham, Canad. J. Chem. Engr., 40 (1962) 263.
6 H. Tagawa, Thermochim. Acta, 80 (1984) 23.
7 P. G. Coombs and Z. A. Munir, in Precious Metals: Mining, Extraction, and Processing, TMS–AIME, Warrendale, PA, 1984, p. 567.
8 Z. A. Munir and P. G. Coombs, Metall. Trans. B., 14B (1983) 95.
9 N. S. Safiullin, J. Appl. Chem. USSR, 32 (1959) 2230.
10 V. V. Pechkovskii, A. G. Zvezdin and S. V. Ostrovskii, J. Appl. Chem. USSR, 36 (1963) 1403.

Zusammenfassung — Anfänglich hydratiertes Eisen(III)-sulfatpulver wurde in Luft im Temperaturbereich 823–923 K zersetzt. Für die Reaktionsordnung des Zersetzungsprozesses, der als Endprodukt festes Fe_2O_3 lieferte, wurde Null und für die Aktivierungsenergie 219 $kJ \cdot mol^{-1}$ ermittelt. Die Art des Produktes und der Kinetik der Zersetzung war in Luft und Argon gleich. Unter den gleichen Bedingungen wurden auch Sulfatproben mit Zusätzen von FeS und Fe_2O_3 zersetzt. Die Ergebnisse bekräftigen sowohl die nullte Reaktionsordnung (im Falle von Fe_2O_3 Zusätzen) als auch einen fehlenden Einfluß von FeS auf die Zersetzung von Eisen(III)-sulfat.

Резюме — Разложение гидратированных порошков сульфата трехвалентного железа было проведено при температуре 823–923 K в воздушной атмосфере. Показано, что реакция разложения, приводящая к образованию твердого оксида трехвалентного железа, имеет нулевой порядок с энергией активации равной 219 кдж·моль$^{-1}$. В атмосфере воздуха и аргона характер образующихся продуктов и кинетика процесса разложения были одинаковыми. Образцы сульфата железа с добавками FeS и Fe_2O_3 были также подвергнуты разложению в аналогичных условиях. Результаты подтвердили нулевой порядок реакции (в случае добавки Fe_2O_3) и отсутствие какого-либо влияния сульфида двухвалентного железа на разложение сульфата железа.