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KINETICS OF THERMAL DECOMPOSITION OF INTERMEDIATE HYDRATES AND BASIC SALTS OF IRON(II) SULPHATE HEPTAHYDRATE

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The kinetics of thermal decomposition of iron(II) sulphate hexa- to monohydrates, as well as the hydroxy- and oxysulphates of iron(III), are presented and discussed. The results confirm that the final intermediate that decomposes to iron(III) oxide and sulphur trioxide during the thermal decomposition of any hydrate of iron(II) sulphate is the oxysulphate, $Fe_2O(SO_4)_2$.

The thermal decomposition of iron(II) sulphate heptahydrate involves the formation of intermediate hydrates and basic salts. Both isothermal and dynamic thermal analysis techniques have proved beyond doubt the formation of the tetrahydrate, the monohydrate, the anhydrous sulphate, the oxysulphate and the hydroxysulphate as the intermediates during the thermal decomposition of various iron(II) sulphate hydrates [1–3]. Though the hexa-, penta-, tri- and dihydrates could not be identified during the thermal decomposition of the various hydrates of iron(II) sulphate, they may be obtained from the heptahydrate by using appropriate procedures [1]. In our earlier communications, an account of the thermal decomposition of various intermediate hydrates [3, 4] and basic sulphates [5] was presented. In the present communication, some kinetic and mechanistic aspects of their thermal decompositions are presented and discussed. For the purpose of kinetic analysis, the method published earlier [6] has been used.

Experimental

The details regarding the materials, apparatus and equipment used, as well as the method of carrying out the experiments, were given earlier [1, 2].

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Results and discussion

For the purpose of kinetic analysis, the decomposition of hydrates of iron(II) sulphate may broadly be divided into three steps:

a) Decomposition to the monohydrate:

$$FeSO_4 \cdot nH_2O = \underset{\text{(intermediate)}}{FeSO_4 \cdot H_2O} + (n-1)H_2O \tag{1}$$

where $n = 2$ to 6.

b) Decomposition of the intermediate monohydrate to the anhydrous sulphate:

$$FeSO_4 \cdot H_2O = FeSO_4 + H_2O \tag{2}$$

c) Decomposition of the intermediate oxysulphate:

$$Fe_2O(SO_4)_2 = Fe_2O_3 + 2SO_3 \tag{3}$$

In the case of the monohydrate, the first step is absent. The oxysulphate is formed as a result of the oxidation of the anhydrous sulphate. A kinetic analysis of the oxidation reaction could not be carried out owing to the lack of sufficient data to calculate α (fraction decomposed).

As the hydroxysulphate is not formed under the present experimental conditions of the thermal decomposition of iron(II) sulphate hydrates, it was prepared separately. Kinetic analysis of the basic sulphates was carried out for the following reactions:

Decomposition of the hydroxysulphate:

$$2Fe(OH)SO_4 = \underset{\text{(intermediate)}}{Fe_2O(SO_4)_2} + H_2O \tag{4}$$

$$\underset{\text{(intermediate)}}{Fe_2O(SO_4)_2} = Fe_2O_3 + 2SO_3 \tag{5}$$

Kinetic analysis was also carried out for the decomposition of an independently prepared sample of the oxysulphate:

$$Fe_2O(SO_4)_2 = Fe_2O_3 + 2SO_3 \tag{6}$$

Table 1 gives a set of typical calculations for the reaction:

$$FeSO_4 \cdot 6H_2O = FeSO_4 \cdot H_2O + 5H_2O \tag{7}$$

Table 2 is a summary of the kinetic data for all the systems studied.

Table 1 A set of typical calculations. System: $FeSO_4 \cdot 6H_2O = FeSO_4 \cdot H_2O + 5H_2O$

				$-\log P(X)$, B, $\bar{B}$ and δ Values for					
Sl. No.	T, K	$\log g(\alpha)$		$E=10$	$E=12$	$E=14$	$E=16$	$E=18$	$E=20$
1	353	−1.918	$-\log_B P(X)$	8.175	9.498	10.798	12.083	13.348	14.810
				6.257	7.580	8.880	10.165	11.430	12.892
2	373	−1.584	$-\log_B P(X)$	8.002	9.294	10.559	11.812	13.052	14.283
				6.418	7.710	8.975	10.228	11.468	12.699
3	413	−0.893	$-\log_B P(X)$	7.523	8.731	9.917	11.090	12.243	13.391
				6.630	7.838	9.024	10.197	11.350	12.498
4	423	−0.723	$-\log_B P(X)$	7.383	8.565	9.725	10.865	11.997	13.118
				6.660	7.842	9.002	10.142	11.274	13.395
5	433	−0.468	$-\log_B P(X)$	7.241	8.402	9.537	10.659	11.765	12.860
				6.773	7.934	9.069	10.191	11.297	12.392
6	443	−0.298	$-\log_B P(X)$	7.110	8.244	9.357	10.458	11.542	12.615
				6.812	7.946	9.059	10.160	11.244	12.317
7	453	−0.129	$-\log_B P(X)$	6.984	8.096	9.186	10.261	11.328	12.380
				6.855	7.967	9.057	10.132	11.199	12.251
			$\bar{B}$	6.629	7.831	9.009	10.174	11.323	12.492
			δ	0.220	0.142	0.066	0.034	0.098	0.228
			$\bar{\delta}$	0.1427					

From the data given in Table 2, it can be seen that the last step of decomposition involving the formation of iron(III) oxide and sulphur trioxide is governed by a D_1 type of diffusion mechanism, irrespective of the starting hydrate. This means that the final step of decomposition is the same in all cases and is independent of the starting hydrate. There is some controversy [1] regarding the final compound that decomposes to iron(III) oxide and sulphur trioxide. According to one view, the final iron(III) compound that decomposes is iron(III) sulphate, while the other view is that the compound is the oxysulphate. Earlier work by the author [7] on the thermal decomposition of iron(III) sulphate gave an activation energy ranging from 247 to 297 kJ/mol, depending on the method of preparation. The oxysulphate, prepared from iron(II) sulphate by the method described earlier [1], decomposes with an activation energy of 148 kCal/mol (619 kJ/mol). The final step of decomposition of $FeSO_4 \cdot nH_2O$ ($n = 1$ to 6) involves an activation energy ranging from 114 to 136 kcal/mol (477 to 569 kJ/mol) (Table 2). From these data it is reasonable to assume that the final compound decomposing is the oxysulphate and not iron(III) sulphate. This conclusion supports our earlier conclusion that the oxysulphate is the final intermediate in the thermal decomposition of hydrated iron(II) sulphates [2–3]. The high energies of activation for this step indicate that the reaction is controlled by the migration of ions to their new lattice positions, rather than by the simple diffusion of SO_3.

Table 2 Kinetic analysis

Sl. No.	Reaction	Activation energy, kcal/mole	Mechanism
	System: $FeSO_4 \cdot 6H_2O$		
1	$FeSO_4 \cdot 6H_2O = FeSO_4 \cdot H_2O + 5H_2O$	14.6 (61.0)*	R_2
2	$FeSO_4 \cdot H_2O = FeSO_4 + H_2O$	21.0 (82.0)	A_2
3	$Fe_2O(SO_4)_2 = Fe_2O_3 + 2SO_3$	127.2 (532)	D_1
	System: $FeSO_4 \cdot 5H_2O$		
4	$FeSO_4 \cdot 5H_2O = FeSO_4 \cdot H_2O + 4H_2O$	16.4 (69)	F_1
5	$FeSO_4 \cdot H_2O = FeSO_4 + H_2O$	16.4 (69)	A_3
6	$Fe_2O(SO_4)_2 = Fe_2O_3 + 2SO_3$	119.8 (500)	D_1
	System: $FeSO_4 \cdot 4H_2O$		
7	$FeSO_4 \cdot 4H_2O = FeSO_4 \cdot H_2O + 3H_2O$	18.0 (75)	F_1
8	$FeSO_4 \cdot H_2O = FeSO_4 + H_2O$	17.0 (71)	A_3
9	$Fe_2O(SO_4)_2 = Fe_2O_3 + 2SO_3$	136.0 (568)	D_1
	System: $FeSO_4 \cdot 3H_2O$		
10	$FeSO_4 \cdot 3H_2O = FeSO_4 \cdot H_2O + 2H_2O$	16.6 (69)	A_2
11	$FeSO_4 \cdot H_2O = FeSO_4 + H_2O$	13.2 (55)	A_2
12	$Fe_2O(SO_4)_2 = Fe_2O_3 + 2SO_3$	114.0 (477)	D_1
	System: $FeSO_4 \cdot 2H_2O$		
13	$FeSO_4 \cdot 2H_2O = FeSO_4 \cdot H_2O + H_2O$	11.0 (46)	A_2
14	$FeSO_4 \cdot H_2O = FeSO_4 + H_2O$	20.6 (86)	A_3
15	$Fe_2O(SO_4)_2 = Fe_2O_3 + 2SO_3$	126.0 (527)	D_1
	System: $FeSO_4 \cdot H_2O$		
16	$FeSO_4 \cdot H_2O = FeSO_4 + H_2O$	13.4 (56)	A_3
17	$Fe_2O(SO_4)_2 = Fe_2O_3 + 2SO_3$	133.0 (556)	D_1
	System: $Fe(OH)SO_4$		
18	$2Fe(OH)SO_4 = Fe_2O(SO_4)_2 + H_2O$ (intermediate)	58.8 (246)	D_2
19	$Fe_2O(SO_4)_2 = Fe_2O_3 + 2SO_3$ (intermediate)	134.0 (560)	D_1
	System: $Fe_2O(SO_4)_2$		
20	$Fe_2O(SO_4)_2 = Fe_2O_3 + 2SO_3$	148.0 (619)	D_1

* kJ/mole

D_1: $g(\alpha) = \alpha^2$; D_2: $g(\alpha) = \alpha + (1 + \alpha)\ln(1 - \alpha)$

F_1: $g(\alpha) = -\ln(1 - \alpha)$; A_2: $g(\alpha) = (-\ln(1 - \alpha))^{\frac{1}{2}}$

A_3: $g(\alpha) = (-\ln(1 - \alpha))^{\frac{1}{3}}$; R_2: $g(\alpha) = 1 - (1 - \alpha)^{\frac{1}{2}}$

The first step of decomposition involving the formation of the monohydrate follows a 'random nucleation' mechanism. In the case of the hexahydrate, however, the step is governed by a phase boundary reaction with cylindrical symmetry. Removal of the last molecule of water involves different mechanisms, depending on the starting hydrate.

The monohydrate is formed during the thermal decomposition of all hydrates, viz. the di- to the heptahydrate. The monohydrate can also be isolated. However, the activation energy required for reaction (2) varies from hydrate to hydrate. Similarly, the oxysulphate is formed as the final intermediate, as shown above during the thermal decomposition of iron(II) sulphate hydrates, as well as during the thermal decomposition of the hydroxysulphate. However, the activation energy of its thermal decomposition varies from case to case. These facts may be explained if it is assumed that these intermediates are formed with excess energy, which varies from case to case, so that the activation energy of decomposition also varies from case to case.

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Zusammenfassung — Die Kinetik der thermischen Zersetzung von Eisen(II)-sulfat-Hexahydrat zum Monohydrat und von Hydroxy- und Oxysulfaten von Eisen(III) ist angegeben und wird diskutiert. Die Ergebnisse bestätigen, daß das letzte, sich zu Eisen(III)-oxid und Schwefeltrioxid zersetzende Zwischenprodukt bei der thermischen Zersetzung aller Hydrate von Eisen(II)-sulfat das Oxysulfat $Fe_2O(SO_4)_2$ ist.

Резюме — Представлена и обсуждена кинетика реакций термического разложения различных гидратов (от гекса- до моногидрата) сульфата железа, а также гидроокиси и оксисульфатов трехвалентного железа. Результаты подтвердили, что промежуточным продуктом разложения какого-либо гидрата сульфата двухвалентного железа является оксисульфат $Fe_2O(SO_4)_2$, разлагающийся затем до окиси трехвалентного железа и трехокиси серы.