

KINETICS OF THE THERMAL DECOMPOSITION OF IRON(II) SULPHATE HEPTAHYDRATE IN AIR

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ABSTRACT

The kinetics of thermal decomposition of iron(II) sulphate heptahydrate were studied using Zsako's statistical method. The thermal decomposition of the heptahydrate consists of three distinct decomposition steps which are amenable to kinetic analysis. These steps are the loss of six molecules of water, the loss of a single molecule of water from the monohydrate, and the decomposition of the intermediate oxysulphate to iron(III) oxide and sulphur trioxide. The process involving the loss of six molecules of water follows Mempel's equation, the loss of a single molecule of water from the monohydrate follows the Avrami equation, and the decomposition of iron(III) oxysulphate follows a parabolic law. The three processes have activation energies of 16, 24 and 132 kcal mole⁻¹ respectively.

INTRODUCTION

Iron(II) sulphate heptahydrate is a waste or by-product formed during pickling of iron and steel, manufacture of titanium dioxide from ilmenite, cementation of copper sulphate by scrap iron, and so on. There is world-wide interest in how to use the large quantities of iron(II) sulphate in its solution form or as the crystallised heptahydrate. As far as the utilisation of the solid is concerned, its main application is in the manufacture of iron oxide red pigment and in the manufacture of iron oxide for subsequent use in the production of iron powder.

A survey of the literature shows that utilisation of the solid heptahydrate involves drying and roasting operations before the end-product (pigment or oxide for reduction) is obtained. Also, the process of dehydration and decomposition to iron(III) oxide is rather complicated involving oxidation of iron(II) to iron(III) and passing through several intermediate steps. Earlier, we reported our observations on the thermal decomposition of the heptahydrate under controlled conditions in air [1,2]. In this communication, we present our results on some kinetic aspects of decomposition.

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Kubo et al. [3] studied the thermal decomposition of iron(II) sulphate heptahydrate and found that the dehydration of the heptahydrate to monohydrate can be expressed by the rate law

$$\frac{d\alpha}{dt} = k_1(1 - \alpha) \quad (1)$$

The dehydration of the monohydrate to anhydrous sulphate was found to obey the rate equation

$$\alpha = k_3 t \quad (2)$$

while the oxidation of anhydrous sulphate followed the rate equation

$$\frac{d\alpha}{dt} = k_2(1 - \alpha) \quad (3)$$

The activation energies for the processes represented by eqns. (1)–(3) were found to be 30, 40 and 32.4 kcal mole⁻¹, respectively. The oxidation of anhydrous sulphate was found to be autocatalytic and to take place at the reactant–product phase boundary. Pechovskii et al. [4] studied the kinetics of thermal decomposition of anhydrous iron(II) sulphate in a McBain balance by heating in a current of air at 680–730°C. The equation of Poginskii and Todes

$$1 - (1 - \alpha)^{1/3} = kt \quad (4)$$

was found to apply satisfactorily. This equation was developed on the assumption of instantaneous formation of nuclei of the new phase on the surface of the initial substance. The slope of the linear plot of $\log \alpha$ vs. $1/T$ gave an activation energy of 60.4 kcal mole⁻¹. Mihalik and Horvath [5] used thermoanalytical methods and found that the decomposition of the iron(II) sulphate to sulphur trioxide was a single-step reaction with zero order and an activation energy of about 60 kcal mole⁻¹. Johnson and Gallagher [6] studied the thermal decomposition kinetics of iron(II) sulphate in oxygen and nitrogen atmospheres. The decomposition in oxygen was found to be a single-step reaction. The data could be explained by the contracting geometry model

$$1 - (1 - \alpha)^{1/n} = kt \quad (5)$$

Activation energies in the range of 45–61 kcal mole⁻¹ were found for various iron(II) sulphate materials prepared and decomposed under different conditions. A kinetic equation was derived for the decomposition of the heptahydrate by Bezilevskii et al. [7]. The use of consecutive reaction analysis for the derivation of kinetic parameters was illustrated for solid state decomposition of iron(II) sulphate by Johnson and Gallagher [8]. Gallagher et al [9] studied the thermal decomposition of reagent grade heptahydrate and freeze-dried iron(II) sulphate monohydrate in oxidising and inert atmospheres and found that the mechanism depended on atmo-

sphere, but is the same for freeze-dried and conventional materials. Rezinik and Ivanov [10] obtained a value of $63.7 \text{ kcal mole}^{-1}$ for the activation energy of the decomposition of $\text{Fe}_2\text{O}(\text{SO}_4)_2$ to Fe_2O_3 .

EXPERIMENTAL

Materials

The iron(II) sulphate heptahydrate required for the investigation was specially prepared starting from Merck analytical reagent grade material. The method was described elsewhere [1].

Apparatus

A derivatograph, supplied by Metrimpex, Hungary, was used in the investigation. It simultaneously records TG, DTG, DTA and T curves on photographic paper.

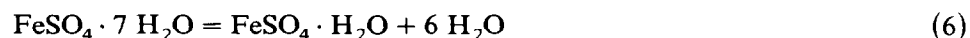
Method

All the experiments were carried out in a dynamic air atmosphere using a heating rate of $10^\circ\text{C min}^{-1}$. Two types of sample holder, one pan and the other cylindrical, were employed. The details of the crucibles were given elsewhere [2]. About 900 mg of the sample was required in the cylindrical holder and 200 mg in the pan type holder. Alumina, ignited at 1200°C , was used as reference substance. The experiments were carried out in the ambient to 1000°C region.

RESULTS AND DISCUSSION

Thermal decomposition studies showed [2] that the results obtained for the decomposition of the heptahydrate in the pan type holders cannot be used for kinetic analysis as the reactions were too complex and overlapping. The results for the thermal decomposition in the cylindrical holders were, however, found to be amenable to kinetic analysis. For the purpose of kinetic analysis, the decomposition of the heptahydrate may be broadly divided into three steps.

(1) Decomposition of the heptahydrate to monohydrate in the temperature range $130\text{--}200^\circ\text{C}$



(2) Decomposition of the monohydrate to the anhydrous sulphate in the

temperature range 330–370°C



(3) Decomposition of the oxysulphate, $\text{Fe}_2\text{O}(\text{SO}_4)_2$, to iron(III) oxide and sulphur trioxide in the temperature range 680–800°C



The oxysulphate is formed as a result of the oxidation of the anhydrous sulphate. A kinetic analysis of the oxidation reaction could not be taken up because the temperature range over which it takes place is too narrow.

We have applied Zsako's statistical method [11] to obtain the experimental activation energies and information on the reaction mechanisms. The values of activation energy thus obtained are compared with those obtained by the method of Dharwadkar and Karkhanawala [12].

In applying Zsako's method, instead of using the relation based on order of reaction

$$f(\alpha) = \alpha^a(1 - \alpha)^b \quad (9)$$

we used the mechanistic equations published widely in the literature. These equations were summarised by Nair and Madhusudanan [13].

In order to calculate the minimum deviation, δ , Zsako tabulated [11] the $-\log p(x)$ values corresponding to different temperatures (100–430°C) and activation energies (10–66 kcal mole⁻¹). We required, however, for the reaction represented by the eqn. (8), $-\log p(x)$ values at higher temperatures and higher activation energies. For this purpose, an approximate equation suggested by Zsako

$$p(x) \approx e^{-x \left(\frac{1}{x^2} - \frac{2}{x^3} \right)} \quad (10)$$

was used and the values for $-\log p(x)$ at different temperatures and activation energies were tabulated [14]. Table 1 gives a set of typical calculations for the reaction represented by eqn. (6). The value of B was calculated using the equation

$$\log g(\alpha) - \log p(x) = B \quad (11)$$

From these B values, the value of minimum deviation, δ , was calculated using the equation:

$$\delta = \sqrt{\frac{\sum (\bar{B} - B_i)^2}{r}} \quad (12)$$

where B_i is the individual B value, \bar{B} is the arithmetic mean of all the B_i values, and r is the number of B values used. Likewise, values for various mechanistic equations were calculated. These minimum values, δ_{\min} , for three mechanistic equations are given in Table 2. The minimum values for the other mechanistic equations were far larger than these values and hence

TABLE 1

A set of typical calculations for the reaction $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O} = \text{FeSO}_4 \cdot \text{H}_2\text{O} + 6 \text{H}_2\text{O}$; $g(\alpha) = 1 - (1 - \alpha)^{1/2}$

T (K)	$\log g(\alpha)$	$-\log p(x)$, B , \bar{B} and δ values	$E = 1 - (1 - \alpha)^{1/2}$							
			$E = 10$	$E = 12$	$E = 14$	$E = 16$	$E = 18$	$E = 20$	$E = 22$	
403	-1.358	$-\log p(x)$ B	7.678 6.320	8.908 7.550	10.121 8.763	11.328 9.960	12.503 11.145	13.672 12.314	14.838 13.480	
413	-1.130	$-\log p(x)$ B	7.523 6.393	8.731 7.601	9.917 8.787	11.090 9.960	12.243 11.113	13.391 12.261	14.530 13.400	
423	-0.860	$-\log p(x)$ B	7.383 6.525	8.565 7.705	9.725 8.865	10.865 10.005	11.997 11.137	13.118 12.258	14.232 13.372	
433	-0.613	$-\log p(x)$ B	7.241 6.628	8.402 7.789	9.537 8.924	10.659 10.046	11.765 11.152	12.860 12.247	13.952 13.339	
443	-0.448	$-\log p(x)$ B	7.110 6.662	8.244 7.796	9.357 8.909	10.458 10.010	11.542 11.094	12.615 12.167	13.681 13.233	
453	-0.307	$-\log p(x)$ B	6.984 6.677	8.096 7.789	9.186 8.879	10.261 9.954	11.328 11.021	12.380 12.073	13.423 13.116	
463	-0.232	$-\log p(x)$ B	6.862 6.630	7.853 7.621	9.025 8.793	10.078 9.846	11.118 10.886	12.153 11.921	13.105 12.873	
473	-0.150	$-\log p(x)$ \bar{B} δ	6.744 6.594 6.553 0.1316	7.818 7.668 7.690 0.0955	8.864 8.714 8.829 0.0755	9.900 9.750 9.941 0.0973	10.923 10.773 11.040 0.1317	11.935 11.785 12.128 0.1884	12.940 12.790 13.200 0.2537	

 $\delta_{\min} = 0.0755$

TABLE 2

Minimum values, δ_{\min} , for three mechanistic equations applied to the equation $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O} = \text{FeSO}_4 \cdot \text{H}_2\text{O} + 6 \text{H}_2\text{O}$

$g(\alpha)$	δ_{\min}	Activation energy, E (kcal mole ⁻¹)
$-\ln(1-\alpha)$	0.0571	16
$1-(1-\alpha)^{1/2}$	0.0755	14
$1-(1-\alpha)^{1/3}$	0.0720	14

min. $\delta_{\min} = 0.0571$

rejected. From the table, it is evident that the minimum value of δ_{\min} is 0.0571 and the corresponding mechanistic equation is $g(\alpha) = -\ln(1-\alpha)$ with a corresponding activation energy of 16 kcal mole⁻¹. A summary of the mechanistic equations along with the activation energies for the three decompositions is given in Table 3.

Figure 1 represents the Dharwadkar and Karkhanawala plots for the same reactions. From the slopes of these straight lines, the activation energies were calculated and are given in Table 3.

As can be seen from Table 3, values for the activation energies obtained by Zsako's method are comparable with those obtained by Dharwadkar and Karkhanawala for the dehydration reactions, while they differ greatly in the case of decomposition of the oxysulphate. Zsako's method has the advantage of giving the mechanism of the reaction at the same time. The process involving the loss of six molecules of water obeys Mempel's equation and the process involving the dehydration of the monohydrate obeys the Avrami equation. Both these equations are based on nucleation as the rate-controlling step. The process of decomposition of the oxysulphate obeys a parabolic law.

TABLE 3

Comparison of activation energies and a summary of data

Reaction	Activation energy (kcal mole ⁻¹)		$g(\alpha)$
	Zsako	Dharwadkar and Karkhanawala	
$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O} = \text{FeSO}_4 \cdot \text{H}_2\text{O} + 6\text{H}_2\text{O}$	16	19	$-\ln(1-\alpha)$
$\text{FeSO}_4 \cdot \text{H}_2\text{O} = \text{FeSO}_4 + \text{H}_2\text{O}$	34	32	$-\ln(1-\alpha)^{1/2}$
$\text{Fe}_2\text{O}(\text{SO}_4)_2 = \text{Fe}_2\text{O}_3 + 2 \text{SO}_3$	132	119	α^2

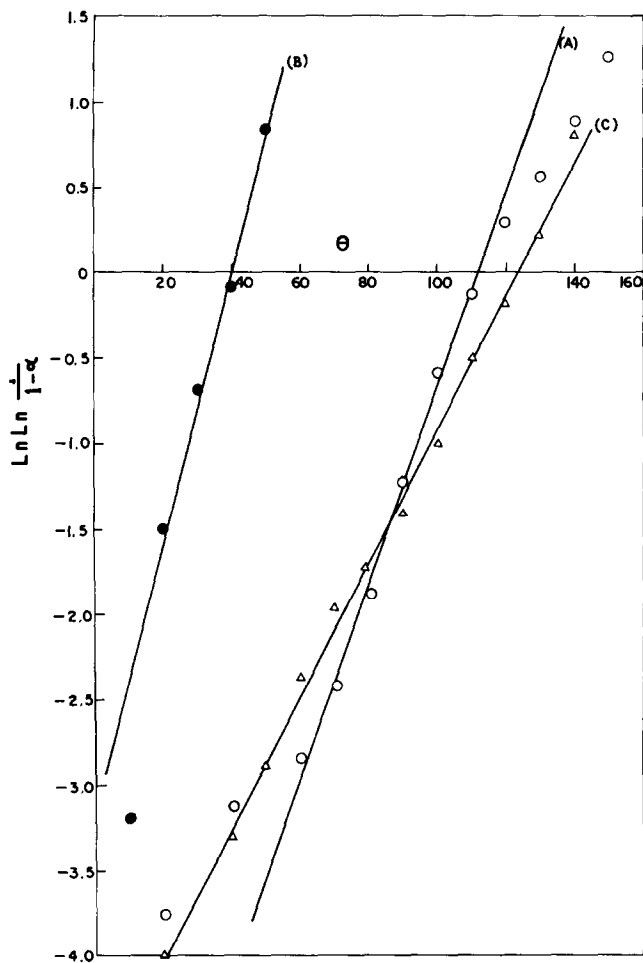
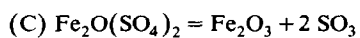
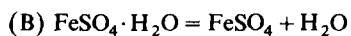
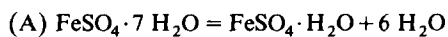


Fig. 1. Plot of $\ln \ln \frac{1}{1-\alpha}$ vs. θ for the decomposition of $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$.



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