KINETICS OF THE THERMAL DECOMPOSITION OF HYDRATES AND BASIC SALTS OF FeSO$_4$

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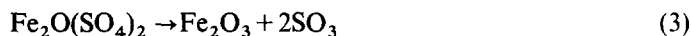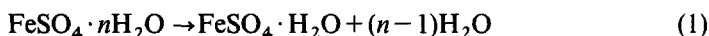REGIONAL RESEARCH LABORATORY BHUBANESWAR–751 013,
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Activation energies for the thermal decomposition reactions of hydrates and basic salts of FeSO$_4$ were calculated using both conventional and statistical methods. The advantage and disadvantage of both methods is brought out. A combined method is proposed.

A study of the kinetics of the thermal decomposition of iron(II) sulphate hydrates and basic salts is of importance in view of the interest shown throughout the world in the utilisation of "waste" iron(II) sulphate heptahydrate. Iron(II) sulphate, when it comes out freshly from various industries, is a heptahydrate, FeSO$_4 \cdot$ 7H$_2$O with small admixtures of free acid (about 1%), moisture, and some other minor impurities. However, on standing, the salt slowly loses water and various intermediate hydrates are formed, depending on the humidity and temperature conditions of the surrounding atmosphere. Along with dehydration, the salt also undergoes some oxidation to iron(III) basic salts. The basic salt identified in this laboratory is a hydroxy salt, Fe(OH)SO$_4$. When heated, the iron(II) sulphate heptahydrate undergoes dehydration to various intermediate hydrates coupled with considerable oxidation. The common intermediate hydrates identified in the literature are the tetra- and the monohydrates together with hydroxy and oxy basic salts [1]. However, other hydrates can be prepared [1] in the laboratory for immediate study.

The author has developed a graphical method [2] for the evaluation of mechanism and activation energies based on a statistical method described by Zsakó [3]. Both Zsakó's and the author's methods give the average activation energy for the whole temperature range studied. If there are any breaks in the kinetic process, for example due to change in mechanism and hence activation energy, such change is not detected by these methods, while they give the mechanism for the whole temperature range. For detecting changes in mechanism earlier methods depending mostly on a first order reaction model, are more suitable.

In view of the above observations, it was felt that the kinetics of thermal decomposition of the hydrates and basic salts may be studied using the conventional methods which permit any breaks in the decomposition process to be detected. For this purpose, therefore, the method of Horowitz and Metzger [4] as modified by Dharwadkar and Karkhanawala [5], was selected. The α-values at various temperatures were obtained from our previous studies [6, 7].

The hydrates of iron(II) sulphate, other than the monohydrate, undergo dehydration in three stages:

$$FeSO_4 \cdot nH_2O \rightarrow FeSO_4 \cdot H_2O + (n-1)H_2O \qquad (1)$$

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

$$Fe_2O(SO_4)_2 \rightarrow Fe_2O_3 + 2SO_3 \qquad (3)$$

In the case of the monohydrate, only reactions (2) and (3) are involved.

Under the conditions of the present set of experiments, where cylindrical crucibles were used, formation of $Fe(OH)SO_4$ does not take place. However, the
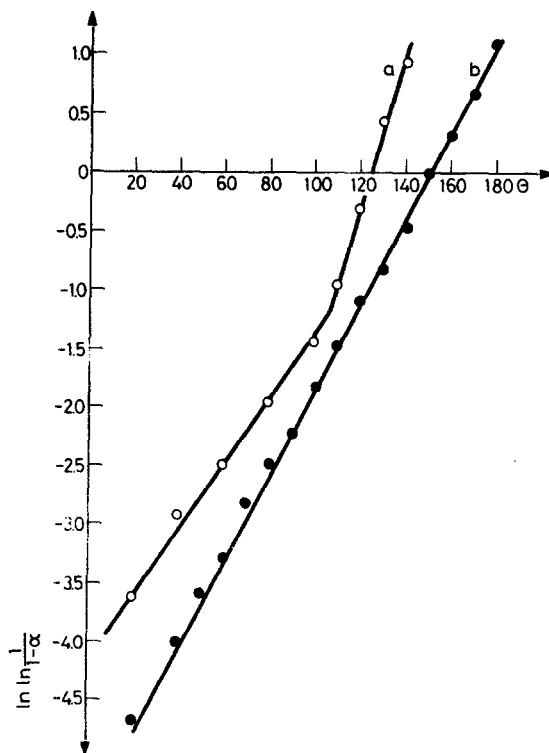

Fig. 1 Plot of $\ln \ln (1/1 - \alpha)$ vs. θ for the reactions: a $-$ $2Fe(OH)SO_4 \rightarrow Fe_2O(SO_4)_2 + H_2O$; b $-$ $Fe_2O(SO_4)_2 \rightarrow Fe_2O_3 + 2SO_3$

Table 1 Activation energies for the thermal decomposition of hydrates and basic salts of $FeSO_4$

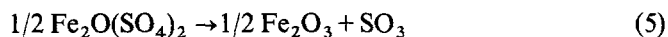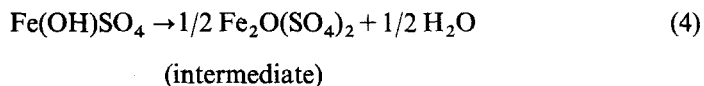| S. No.	Reaction		E, kJ/mol	
			D & K method	author's method
System I				
1	$FeSO_4 \cdot 7H_2O$	$= FeSO_4 \cdot H_2O + 6H_2O$	79.00	71.00
2	$FeSO_4 \cdot H_2O$	$= FeSO_4 + H_2O$	134.00	146.00
3	$Fe_2O(SO_4)_2$	$= Fe_2O_3 + 2SO_3$	497.00	560.00
System II				
4	$FeSO_4 \cdot 6H_2O$	$= FeSO_4 \cdot H_2O + 5H_2O$	63.00	61.00
5	$FeSO_4 \cdot H_2O$	$= FeSO_4 + H_2O$	142.00	82.00
6	$Fe_2O(SO_4)_2$	$= Fe_2O_3 + 2SO_3$	493.00	532.00
System III				
7	$FeSO_4 \cdot 5H_2O$	$= FeSO_4 \cdot H_2O + 4H_2O$	75.00	69.00
8	$FeSO_4 \cdot H_2O$	$= FeSO_4 + H_2O$	134.00	69.00
9	$Fe_2O(SO_4)_2$	$= Fe_2O_3 + 2SO_3$	506.00	500.00
System IV				
10	$FeSO_4 \cdot 4H_2O$	$= FeSO_4 \cdot H_2O + 3H_2O$	75.00	75.00
11	$FeSO_4 \cdot H_2O$	$= FeSO_4 + H_2O$	163.00	71.00
12	$Fe_2O(SO_4)_2$	$= Fe_2O_3 + 2SO_3$	493.00	568.00
System V				
13	$FeSO_4 \cdot 3H_2O$	$= FeSO_4 \cdot H_2O + 2H_2O$	75.00	69.00
14	$FeSO_4 \cdot H_2O$	$= FeSO_4 + H_2O$	109.00	55.00
15	$Fe_2O(SO_4)_2$	$= Fe_2O_3 + 2SO_3$	514.00	477.00
System VI				
16	$FeSO_4 \cdot 2H_2O$	$= FeSO_4 \cdot H_2O + H_2O$	50.00	46.00
17	$FeSO_4 \cdot H_2O$	$= FeSO_4 + H_2O$	134.00	86.00
18	$Fe_2O(SO_4)_2$	$= Fe_2O_3 + 2SO_3$	514.00	527.00
System VII				
19	$FeSO_4 \cdot H_2O$	$= FeSO_4 + H_2O$	138.00	56.00
20	$Fe_2O(SO_4)_2$	$= Fe_2O_3 + 2SO_3$	531.00	556.00
System VIII				
21	$Fe(OH)SO_4$	$= 1/2\ Fe_2O(SO_4)_2 + H_2O$	151.00	246.00
22	$Fe_2O(SO_4)_2$	$= Fe_2O_3 + 2SO_3$	510.00	560.00
System IX				
23	$Fe_2O(SO_4)_2$	$= Fe_2O_3 + 2SO_3$	556.00	619.00

kinetics of the thermal decomposition of this salt, prepared separately, are given here to make the investigation complete.

$Fe_2O(SO_4)_2$ of reaction (3) comes from the oxidation of the anhydrous sulphate of reaction (2). However, the kinetic analysis of the oxidation of the anhydrous

sulphate to the oxysulphate could not be done owing to the lack of sufficient data for calculation of "α".

The decomposition of the hydroxy sulphate is represented as:

$$Fe(OH)SO_4 \rightarrow 1/2\ Fe_2O(SO_4)_2 + 1/2\ H_2O \qquad (4)$$

(intermediate)

$$1/2\ Fe_2O(SO_4)_2 \rightarrow 1/2\ Fe_2O_3 + SO_3 \qquad (5)$$

The decomposition of oxysulphate is represented as:

$$Fe_2O(SO_4)_2 \rightarrow Fe_2O_3 + 2SO_3 \qquad (6)$$

The activation energies of thermal decompositions were obtained from the plots of $\ln\ln(1/1-\alpha)$ vs. θ (D & K method) as well as using the statistical method of the author referred to above. It has been found that except in the case of the thermal decomposition of $Fe(OH)SO_4$, in all other cases straight line relations were obtained for the entire temperature range without any breaks. However, in the case of the thermal decomposition of the hydroxy sulphate, $Fe(OH)SO_4$, the first reaction (4), involving the formation of the intermediate, shows a break in the kinetic curve indicating a change in mechanism (Fig. 1). Thus the D&K (or any similar method) method alone cannot give the kinetic model (mechanism) though it predicts the change in mechanism. Statistical methods give the mechanism over the entire temperature range of reaction but cannot predict any change in mechanism. It is, therefore, advisable to first draw the kinetic curves using a conventional method and then analyse the different portions of the curve by the statistical methods.

From Table 1 it is evident that the agreement between the two methods is not always satisfactory. It is because the D&K method does not take into consideration various mechanisms for the evaluation of the activation energy.

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