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# THERMAL DECOMPOSITION OF IRON(II) SULPHATE HEPTAHYDRATE IN AIR IN THE PRESENCE OF CALCIUM, STRONTIUM AND BARIUM CARBONATES

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The thermal decomposition in air of iron(II) sulphate heptahydrate in the presence of calcium, strontium and barium carbonates has been carried out. The decomposition path varies from carbonate to carbonate. Also, these decompositions are different from those of basic beryllium carbonate and basic magnesium carbonate. The results obtained for the kinetics of thermal decomposition have also been presented.

As a part of studies on waste utilization, investigations were carried out by the author over the past several years resulting in both basic and applied work on the utilisation of iron(II) sulphate heptahydrate. Much of the basic work has already been published. As far as double decomposition reactions involving alkali and alkaline earth carbonates are concerned, three papers on reactions involving alkali carbonates [1], basic beryllium carbonate [2] and basic magnesium carbonate have appeared [3]. During the course of these investigations, it was found that the nature of decomposition of iron(II) sulphate heptahydrate depends on the alkali used. We regarded interesting to study the thermal decomposition of the heptahydrate in the presence of the rest of the alkaline earth carbonates. An account of these investigations is presented in this paper.

## Experimental

### *Materials*

Iron(II) sulphate heptahydrate was prepared and analyzed as described earlier [4]. Calcium, strontium and barium carbonates were of Analytical Reagent grade.

Apparatus and methods: As described in the preceding communication [3].

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## Results and discussion

The thermal decomposition of iron(II) sulphate heptahydrate in the presence of calcium carbonate is shown in Fig. 1. Curve (a) represents the thermal decomposition of the mixture while curves (b) and (c) represent that of calcium carbonate and calcium sulphate, respectively. The thermal decomposition curves may conveniently be divided into four major regions of weight loss. In the first region (60–200°) the weight loss (Table 1) is due to the following reaction:

$$FeSO_4 \cdot 7H_2O = FeSO_4 \cdot H_2O + 6H_2O \quad (1)$$

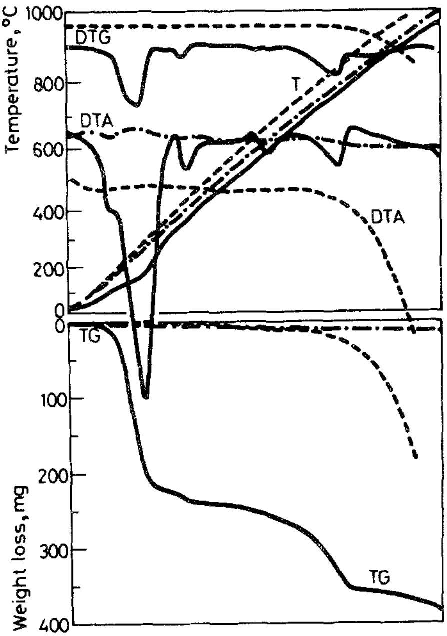

**Fig. 1** Thermal decomposition of iron(II) sulphate heptahydrate in the presence of calcium carbonate. —— $FeSO_4 \cdot 7H_2O + CaCO_3$; – – – $CaCO_3$; –.–.– $CaSO_4$

In the second region (200–380°) the monohydrate formed by the reaction (1) loses its water molecule:

$$FeSO_4 \cdot H_2O = FeSO_4 + H_2O \quad (2)$$

However, the observed (7.52%) weight loss does not agree well with the calculated (10.59%) weight loss. This is attributed to the partial oxidation of iron(II) to iron(III) [5, 6] leading to weight gain. The anhydrous salt is oxidized in

**Table 1** Thermal decomposition of the heptahydrate in the presence of calcium carbonate

| Sl. No. | Temp. range, °C | Probable reaction | Peak (DTA), °C | Weight loss, % | |
|---|---|---|---|---|---|
| | | | | calcd. | obsd. |
| 1 | 60–200 | $FeSO_4 \cdot 7H_2O = FeSO_4 \cdot H_2O + 6H_2O$ | 170 | 38.85 | 39.28 |
| 2 | 200–380 | $FeSO_4 \cdot H_2O = FeSO_4 + H_2O$ | 350 | 10.59 | 7.52 |
| 3 | 460–600 | $2FeSO_4 + 1/2\,O_2 = Fe_2O(SO_4)_2$ | 550 | +5.26 | −5.60* |
| 4 | 600–780 | a) $Fe_2O(SO_4)_2 = Fe_2O_3 + 2SO_3$<br>b) $CaCO_3 = CaO + CO_2$ | | ** | |

* Slight reaction of iron(II) or iron(III) oxysulphate with $CaCO_3$. ** Not calculated as the thermal decomposition is incomplete.

the region 380–460° slowly but its oxidation become faster in the region 460–600° and is accompanied by an exothermic peak at 520°. However, the TG curve in the region mentioned above does not show any weight gain presumably due to some sort of reaction between the anhydrous salt and/or oxysulphate (formed by the oxidation of the anhydrous salt) with calcium carbonate. The material taken out around 450° does not show the presence of calcium sulphate by X-ray diffraction analysis thus indicating the small extent of the reaction and the consequent escape of small amount of the calcium sulphate from detection. The X-ray examination of the intermediate compounds at higher temperatures also failed to show the presence of calcium sulphate. It is, therefore, presumed that: (1) the anhydrous salt is oxidized to oxysulphate and does not react with calcium carbonate and (2) the oxysulphate is preferably decomposed to iron(III) oxide and does not react with calcium carbonate, even though in both cases, probably there is some reaction with calcium carbonate. The weight loss in the region 600–780°, therefore, involves the decomposition of the oxysulphate (Table 1) along with that of $CaCO_3$:

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

$$CaCO_3 = CaO + CO_2 \tag{4}$$

The X-ray data of the final decomposition compound at 980° show the presence of $Fe_2O_3$, $CaCO_3$ and CaO (Table 5) indicating that the components of the mixture decomposed independently and also that the decomposition of the calcium carbonate is not complete at this temperature.

Figure 2 represents the thermal decomposition of the heptahydrate in the presence of strontium carbonate. Table 2 gives the data on weight loss/gain observed with probable assignment to reactions involved. Curve (a), (b) and (c) of Figure 2 represent, respectively, the thermal decomposition of the mixture, strontium carbonate and strontium sulphate.

**Table 2** Thermal decomposition of $FeSO_4 \cdot 7H_2O$ in the presence of $SrCO_3$

| Sl. No. | Temp. region, °C | Peak temp., °C | Probable reaction | Weight loss, % | | Remarks |
|---|---|---|---|---|---|---|
| | | | | obsd. | calcd. | |
| 1 | 60–100 | 100 (inflexion) | $FeSO_4 \cdot 7H_2O = FeSO_4 \cdot 4H_2O + 3H_2O$ | 7.34 | 19.42 | 1 |
| 2 | 60–240 | 160 (endo) | $FeSO_4 \cdot 7H_2O = FeSO_4 + 7H_2O$ | 52.27 | 45.32 | 2 |
| 3 | 240–380 | 320 (exo) | $FeSO_4 + SrCO_3 + 1/4\,O_2 = 1/2\,Fe_2O_3 + SrSO_4 + CO_2$ | 7.85 | 14.31 | 3 |

*Remarks:*

1. Reaction incomplete. Tetrahydrate starts decomposing soon after its formation.
2. Major reaction. The higher observed weight loss is attributed to the reaction between the components.
3. The large difference between the calculated and the observed losses is attributed to part of the reaction occurring in the previous step.

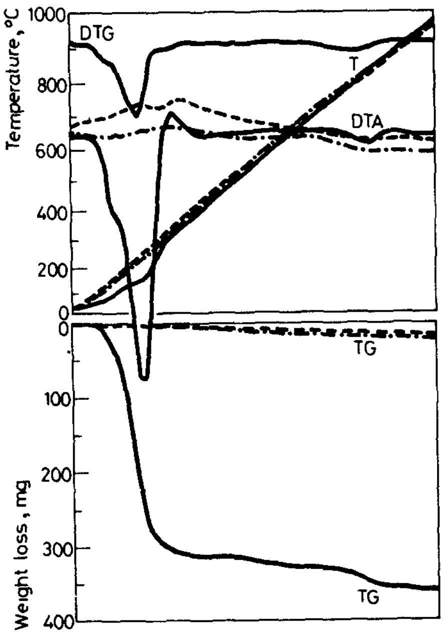

**Fig. 2** Thermal decomposition of iron(II) sulphate heptahydrate in the presence of strontium carbonate.
—— $FeSO_4 + SrCO_3$; – – – $SrCO_3$; – · – · – $SrSO_4$

The DTA curve shows an inflexion at 100° and represents the formation of the iron(II) sulphate tetrahydrate and its immediate dehydration along with the heptahydrate. This, however, can not be attributed to the melting of $FeSO_4 \cdot 7H_2O$ as the sample taken out at this temperature did not show any sign of melting. Considering the region, 60–240° with an endothermic DTA peak at 160°, no simple reaction can be assumed in this region to account for the observed weight loss. The major reaction may be assumed as:

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

The excess loss over the calculated (Table 2) is accounted for by the reaction between the iron(II) sulphate and strontium carbonate:

$$FeSO_4 + SrCO_3 + 1/4\,O_2 = 1/2\,Fe_2O_3 + SrSO_4 + CO_2 \tag{6}$$

Reaction 6 is considered to be a combination of the following reactions:

$$FeSO_4 + SrCO_3 = FeCO_3 + SrSO_4 \tag{7}$$

$$FeCO_3 + H_2O = Fe(OH)_2 + CO_2 \tag{8}$$

$$Fe(OH)_2 = FeO + H_2O \tag{9}$$

$$3FeO + 1/2O_2 = Fe_3O_4 \tag{10}$$

$$2Fe_3O_4 + 1/2\,O_2 = 3Fe_2O_3 \tag{11}$$

The reaction mixture taken out around 240°, contained X-ray lines due to $SrSO_4$ ($d$ = 2.97, 3.77, 3.43 Å). The mixture also has greenish black colour indicating the presence of iron(II) hydroxide. In the region 240–380° the main reaction is the one represented by equation (6). Reaction represented by equation (11) is responsible for the exothermic peak at 320°. The mixture taken out at 380° was found to be non-magnetic and did not contain iron(II) confirming above reactions. The large difference between the observed and calculated weight loss for reaction (6) (Table 2) is attributed to the loss of weight that occurs in the previous step.

From Figure 2, it is evident that strontium carbonate and strontium sulphate do not lose weight in the entire region studied. However, the DTA curve shows endothermic peak and the TG curve shows weight loss in the 750–850° region. This may be attributed to the formation of strontium ferrite:

$$SrCO_3 + Fe_2O_3 = SrFe_2O_4 + CO_2 \tag{12}$$

X-ray diffraction analysis of the final compound of double decomposition reaction showed the presence of iron(III) oxide, strontium sulphate and strontium ferrite (Table 5).

The kinetics of thermal decomposition were worked out for the portion of the TG curve representing the double decomposition reaction. The reaction follows a diffusion controlled path with an activation energy of 124 kJ/mol.

Figure 3 represents the thermal decomposition of the heptahydrate in the presence of barium carbonate. The corresponding weight loss data are presented in Table 3.

The first break in the DTA curve can be observed at 110° in the form of an inflexion. This is attributed to the incomplete dehydration of the heptahydrate to the tetrahydrate as the tetrahydrate starts dehydrating immediately after its formation. If we take the temperature region 60–240°, with an endothermic peak at 180°, the reaction that is taking place can be represented by equation (1). The observed and calculated weight losses for this reaction agree well (Table 3).

The reaction taking place in the 240–380° region can be explained by equation (2). The calculated and observed weight losses, however, do not agree fairly well for this reaction, but this can be explained by: (a) overlapping of reactions (1) and (2) and (b) partial oxidation of iron(II) to iron(III).

In the temperature range 540–750° the following reactions are expected:

$$FeSO_4 + BaCO_3 = FeCO_3 + BaSO_4 \text{ (endothermic)} \qquad (13)$$

$$2FeCO_3 + 1/2\,O_2 = Fe_2O_3 + 2CO_2 \text{ (exothermic)} \qquad (14)$$

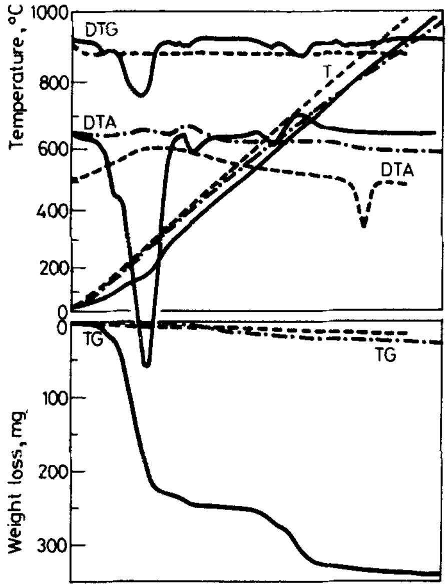

Fig. 3 Thermal decomposition of iron(II) sulphate heptahydrate in the presence of barium carbonate. —— $FeSO_4 + BaCO_3$; – – – $BaCO_3$; –.–.–.– $BaSO_4$

**Table 3** Thermal decomposition of $FeSO_4 \cdot 7H_2O$ in the presence of $BaCO_3$

| Sl. No. | Temp. region, °C | Peak temp., °C | Probable reaction | Weight loss, % obsd. | Weight loss, % calcd. | Remarks |
|---|---|---|---|---|---|---|
| 1 | 60–110 | 110 (inflexion) | $FeSO_4 \cdot 7H_2O = FeSO_4 \cdot 4H_2O+ +3H_2O$ | 4.59 | 19.42 | 1 |
| 2 | 60–240 | 180 (endo) | $FeSO_4 \cdot 7H_2O = FeSO_4 \cdot H_2O+ +6H_2O$ | 40.36 | 38.85 | 2 |
| 3 | 240–380 | 360 (endo) | $FeSO_4 \cdot H_2O = FeSO_4+H_2O$ | 7.69 | 10.59 | 3 |
| 4 | 540–750 | 590 (endo) | $FeSO_4 \cdot BaCO_3+1/4\,O_2=$ | 24.00 | 26.21 | 4 |
|  |  | 670 (exo) | $BaSO_4+1/2\,Fe_2O_3+CO_2$ |  |  |  |

*Remarks:*

1. The reaction is not complete. The tetrahydrate starts decomposing soon after its formation.

2, 3, 4 Please see text for explanation.

**Table 4** Kinetics of thermal decomposition of $FeSO_4 \cdot 7H_2O$ in the presence of barium carbonate

| Sl. No. | Reaction | E, kJ/mol | Mech. Eq. | Model |
|---|---|---|---|---|
| 1 | $FeSO_4 \cdot 7H_2O = FeSO_4 \cdot H_2O+6H_2O$ | 76.00 | $1-(1-\alpha)^{1/2}$ | 1 |
| 2 | $FeSO_4 \cdot H_2O = FeSO_4+H_2O$ | 71.00 | $1-(1-\alpha)^{1/3}$ | 2 |
| 3 | $FeSO_4+BaCO_3+1/4\,O_2=1/2\,Fe_2O_3+ +CO_2+BaSO_4$ | 275.00 | $\alpha^2$ | 3 |

1. Phase boundary reactions-cylindrical symmetry-movement of interface.
2. Phase boundary reaction-assumes spherical symmetry.
3. One dimensional diffusion with constant diffusion coefficient.

so that the overall reaction is the following:

$$FeSO_4+BaCO_3+1/4\,O_2 = 1/2\,Fe_2O_3+BaSO_4+CO_2 \qquad (15)$$

Reaction (13) is responsible for the endothermic peak at 590° and reaction (14) is represented by the exothermic peak at 670°. The calculated and the observed weight losses for reaction (14) agree fairly well. The reaction between $FeCO_3$ and $H_2O$ is ruled out in this case due to the high temperature involved where water vapour does not exist in the vicinity of the sample.

The kinetic analysis was carried out for all the three types of reactions and the data are presented in Table 4.

**Table 5** Thermal decomposition of $FeSO_4 \cdot 7H_2O$ in the presence of $CaCO_3$, $SrCO_3$ & $BaCO_3$ XRD data for the final compound

| Obsd. '*d*' values with intensities in parentheses | | | | Assignment | | |
|---|---|---|---|---|---|---|
| Sl. No. | System I | System II | System III | System I | System II | System III |
| 1 | 3.66 (40) | 3.77 (30) | 4.35 (50) | $\alpha$-$Fe_2O_3$ | $SrSO_4$ | $BaSO_4$ |
| 2 | 3.58 (60) | 3.63 (30) | 3.89 (50) | $CaCO_3$ | $SrCO_3$ | $BaSO_4$ |
| 3 | 3.30 (100) | 3.43 (30) | 3.77 (100) | $CaCO_3$ | $SrSO_4$ | $BaSO_4$ |
| 4 | 3.03 (20) | 3.29 (10) | 3.72 (50) | $CaCO_3$ | $SrSO_4$ | $BaCO_3$ |
| 5 | 2.69 (80) | 3.17 (30) | 3.66 (30) | $\alpha$-$Fe_2O_3$ | $SrSO_4$ | $\alpha$-$Fe_2O_3$ |
| 6 | 2.51 (40) | 2.97 (100) | 3.57 (30) | $\alpha$-$Fe_2O_3$, $CaCO_3$ | $SrSO_4$ | $BaSO_4$ |
| 7 | 2.41 (40) | 2.75 (50) | 3.44 (80) | CaO | $SrFe_3O_4$ | $BaSO_4$ |
| 8 | 2.19 (20) | 2.70 (100) | 3.17 (30) | $\alpha$-$Fe_2O_3$ | $\alpha$-$Fe_2O_3$ | $BaSO_4$ |
| 9 | 1.70 (20) | 2.68 (30) | 3.13 (50) | CaO | $SrSO_4$ | $BaFe_2O_4$ |
| 10 | 1.48 (20) | 2.54 (50) | 2.70 (100) | $\alpha$-$Fe_2O_3$ | $\alpha$-$Fe_2O_3$, $SrCO_3$ | $\alpha$-$Fe_2O_3$ |
| 11 | 1.45 (20) | 2.20 (30) | 2.51 (30) | $\alpha$-$Fe_2O_3$ | $\alpha$-$Fe_2O_3$ | $\alpha$-$Fe_2O_3$ |
| 12 | — | 1.95 (10) | 2.11 (30) | — | $SrFe_2O_4$ | $BaSO_4$ |
| 13 | — | 1.84 (30) | — | — | $\alpha$-$Fe_2O_3$ | — |

Prominent lines of:

1. $CaSO_4$: 3.49 (100), 2.85 (35), 2.33 (20), 6.05 (100), 3.01 (90), 2.80 (90)
2. $SrSO_4$: 3.62 (100), 3.30 (98), 2.97 (100), 2.73 (63), 2.54 (40), 2.17 (14)
3. $BaSO_4$: 4.35 (30), 3.77 (100), 3.44 (100), 3.10 (97), 2.65 (65), 2.12 (80)
4. $SrFe_2O_4$: 3.08 (34), 2.75 (100), 1.59 (100), 1.95 (34)
5. $BaFe_2O_4$: 3.13 (100), 3.16 (65), 2.74 (40), 7.73 (10)
6. $\alpha$-$Fe_2O_3$: 2.70 (100), 2.54 (50), 2.20 (30), 1.84 (30)
7. $CaCO_3$: 3.58 (100), 3.30 (100), 3.02 (100), 2.51 (100)
8. CaO: 2.41 (100), 1.70 (45), 2.78 (34).

Literature references (ASTM File Nos): $CaSO_4$: 6–226, 2–134; $CaCO_3$: 17–763, 13–192, 5–453, 586; $SrSO_4$: 5–593, 14–467; $BaSO_4$: 5–448, 14–465; $SrFe_2O_4$: 1–1027; $BaFe_2O_4$: 20–132; CaO: 4–777. N.B.: Figures in the parentheses represent intensities.

The X-ray diffraction data for the final compound of decomposition indicate the presence of $BaSO_4$, $Fe_2O_3$ and minor amounts of barium ferrite (Table 5).

From the results obtained so far, it is evident that the three carbonates studied behave differently in their reaction with the heptahydrate. The reaction between iron(II) sulphate, respectively, its oxidation product and calcium carbonate is negligible. The components decompose independently. In this respect, the system resembles the $FeSO_4 \cdot 7H_2O + BeCO_3 \cdot Be(OH)_2$ system. The reaction between strontium carbonate and the heptahydrate starts before the dehydration is complete. In the case of barium carbonate the reaction starts after the dehydration is complete. Also, the oxidation of iron(II) to iron(III) occurs by different mechanisms in the last two cases. In the case of strontium carbonate, the reactions involving the oxidation of $Fe_3O_4$ to $Fe_2O_3$ occur while in the case of barium carbonate, the $FeCO_3$ formed is oxidized directly to $Fe_2O_3$.

* * *

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**Zusammenfassung** — Das Heptahydrat von Eisen-(II)-sulfat wurde in Gegenwart von Calzium-, Strontium- und Bariumcarbonat an Luft zersetzt. Der Verlauf der Zersetzung ist von Carbonat zu Carbonat verschieden. Diese Zersetzungen unterscheiden sich auch von denen mit basischem Beryllium- und Magnesiumcarbonat. Außerdem werden die für die kinetischen Eigenschaften erhaltenen Ergebnisse der thermischen Zersetzung dargestellt.

**Резюме** — Проведено термическое разложение в атмосфере воздуха гептагидрата сульфата двухвалентного железа в присутствии карбонатов кальция, стронция и бария. Характер его разложения изменяется в зависимости от типа карбоната и отличается от такового для основных карбонатов бериллия и магния. Представлены также кинетические результаты термического разложения.