THERMAL DECOMPOSITION OF IRON(II) SULPHATE HEPTAHYDRATE IN THE PRESENCE OF ALKALI METAL CARBONATES

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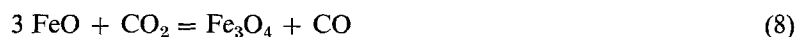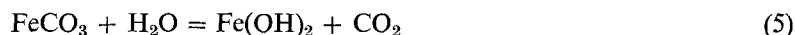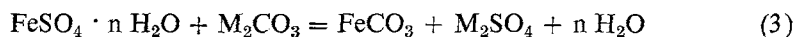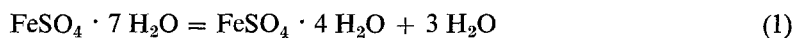
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The thermal decomposition of iron(II) sulphate heptahydrate was carried out in air under dynamic conditions in the presence of lithium, sodium, potassium and rubidium carbonates. The decomposition path in the presence of lithium carbonate differs from that in the presence of the other carbonates. In the presence of lithium carbonate, the heptahydrate loses all the water molecules before entering into reaction with the carbonate. The anhydrous sulphate then reacts with the carbonate, presumably to form iron(II) carbonate, which in turn undergoes decomposition — oxidation via magnetic oxide to ferric oxide. In the case of the other carbonates, iron(II) sulphate enters into reaction with the carbonate in question even before dehydration is complete, to form ferrous carbonate, which in turn reacts with the moisture still present to form green iron(II) hydroxide. This compound then undergoes decomposition — oxidation reactions via magnetic oxide to ferric oxide.

In previous communications we have reported results on the thermal decomposition of various hydrates of iron(II) sulphate in air [1—3]. In this communication, we present results on the thermal decomposition in air of iron(II) sulphate heptahydrate in the presence of alkali metal carbonates.

Various reactions that are most probable to occur during the thermal decomposition process are:

$$FeSO_4 \cdot 7 H_2O = FeSO_4 \cdot 4 H_2O + 3 H_2O \tag{1}$$

$$FeSO_4 \cdot 4 H_2O = FeSO_4 + 4 H_2O \tag{2}$$

$$FeSO_4 \cdot n H_2O + M_2CO_3 = FeCO_3 + M_2SO_4 + n H_2O \tag{3}$$

$$FeCO_3 = FeO + CO_2 \tag{4}$$

$$FeCO_3 + H_2O = Fe(OH)_2 + CO_2 \tag{5}$$

$$Fe(OH)_2 = FeO + H_2O \tag{6}$$

$$3 FeO + \tfrac{1}{2} O_2 = Fe_3O_4 \tag{7}$$

$$3 FeO + CO_2 = Fe_3O_4 + CO \tag{8}$$

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8*

$$2 Fe_3O_4 + \tfrac{1}{2} O_2 = 3 Fe_2O_3 \qquad\qquad (9)$$

Where M = an alkali metal

Thus, the expected final products of decomposition are iron(III) oxide, alkali metal sulphate and small amounts of alkali metal ferrite and alkali metal carbonate and/or oxide.

Experimental

Materials

Analytical reagent grade iron(II) sulphate heptahydrate was dissolved in warm 2 N sulphuric acid to make a saturated solution, and filtered. To the filtrate, absolute alcohol (about half the volume of the filtrate) was added with stirring and the mixture was allowed to cool. The crystallized salt was filtered through a sintered glass funnel and washed several times with small portions of absolute alcohol. The crystals were dried by pressing between the folds of a filter paper, and then by passing a stream of pure carbon dioxide over the sample in a bottle. The bottle was next stoppered. The sample thus prepared and preserved remains unchanged for over 30 days. A representative analysis showed: water content, 7.02 $\pm$ 0.01; sulphate content, 34.32 $\pm$ 0.2% (theor. 34.55%); iron as Fe, 20.1 $\pm$0.1% (theor. 20.1%); free acid, trace.

The specifications of the other materials are as follows: lithium carbonate, B.D.H., 99% pure; sodium carbonate, B.D.H., 99.9% pure; potassium carbonate, "Baker Analysed", 99.9% pure; rubidium carbonate, B.D.H., 99.9% pure.

Apparatus

Thermal decomposition studies were carried out using the OD-102 derivatograph supplied by Metrimpex, Budapest, Hungary. The instrument records simultaneously and photographically thermogravimetric (TG), differential thermal analysis (DTA), derivative thermogravimetric (DTG) and temperature (T) curves. Cylindrical sample holders made of 'platinel' alloy, supplied with the instrument, were used. The ΔT signal was recorded at arbitrary 'sensitivities' marked on the instrument. A heating rate of 10°/min was employed. The temperature of the sample was recorded. A Philips X-ray unit (photographic) was used to obtain the diffraction data.

Method

The requisite quantity (actual amounts are shown in the Figures) of iron(II) sulphate heptahydrate, together with a 5% stoichiometric excess of the carbonate under study (both the materials passing through a 100 mesh sieve), was taken in a small weighing bottle and the contents were mixed thoroughly by rotating the bottle in an inclined position. A stainless steel spatula was held in the bottle to act as a baffle, for effective mixing. The mixing was carried out for 30 minutes. A known amount of the mixture was then transferred into the specimen crucible and packed

by tapping gently a few times. The reference material used was calcined alpha-alumina.

To analyse the intermediate products, separate runs were made in which the samples were heated under identical conditions to the temperature of interest and withdrawn for analysis. All weight loss calculations were performed with respect to the heptahydrate present in the mixture, to facilitate direct comparison with the pure heptahydrate.

Results and discussion

The decomposition of iron(II) sulphate heptahydrate was carried out in the presence of lithium, sodium, potassium or rubidium carbonates. The termal decomposition curves are given in Figs 1 to 4, respectively. The individual decomposition curves of the corresponding carbonates and sulphates are also given in the same Figures. Examination of these Figures reveals that the thermal decomposition curve in the presence of lithium carbonate differs markedly from the other curves, but resembles that for pure iron(II) sulphate heptahydrate up to 200°. All the curves show an inflexion in the region $60-120°$, which by analogy with the pure salt is attributed to the formation of the tetrahydrate (equation 1). However, the observed
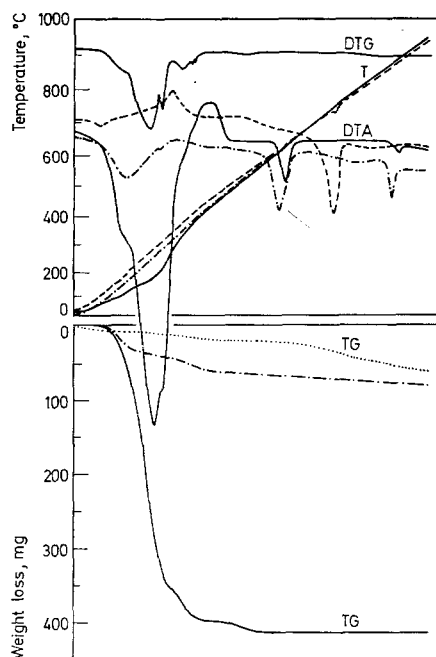

Fig. 1. Thermal decomposition of $FeSO_4 \cdot 7 H_2O$ in air in the presence of Li_2CO_3. ————— $FeSO_4 \cdot 7 H_2O + Li_2CO_3$; ------ Li_2CO_3; —·—·—·— Li_2SO_4. Weight of mixture: 897.48 mg, weight of sulphate: 701.92 mg; weight of carbonate: 195.56 mg

weight loss (Li, 35.0; Na, 7.0; K, 40.0; and Rb, 45.0 mg) is far less than the calculated weight loss (136.34, 107.0, 105.17 and 101.0 mg, respectively) as required by equation (1). The reason ascribed to this is the same as was forwarded in the case of the heptahydrate [4]: part of the liberated water is retained by the molten tetrahydrate.

The next region of interest is that between 100 and 200°. In this region the decomposition path of the heptahydrate in the presence of lithium carbonate is different
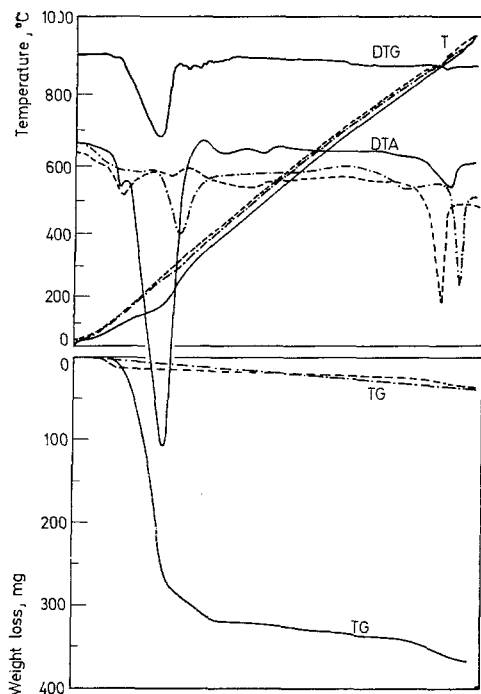

Fig. 2. Thermal decomposition of $FeSO_4 \cdot 7 H_2O$ in air in the presence of Na_2CO_3. ——— $FeSO_4 \cdot 7 H_2O + Na_2CO_3$; ------ Na_2CO_3; —·—·—·— Na_2SO_4; weight of mixture: 874.47 mg; weight of sulphate: 550.95 mg; weight of carbonate: 323.52 mg

from those in the presence of the other carbonates. In the presence of lithium carbonate, the observed weight loss far exceeds the calculated one, but the total weight loss up to 200° (i.e. 60—500°) conforms with the reaction:

$$FeSO_4 \cdot 7 H_2O (+ Li_2CO_3) = FeSO_4 + 7 H_2O (+ Li_2CO_3) . \qquad (10)$$
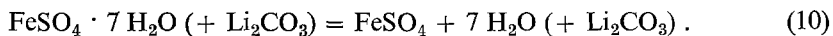
The calculated and observed weight losses are 318 and 325 mg, respectively. This is because the water retained in the initial stages is given off in the later stages (presumably without any reaction between the heptahydrate and the carbonate) along with the remaining water molecules.

The situation in the presence of the other carbonates, however, is not the same. The observed weight losses in the region $60-200°$ (sodium carbonate, 270.0; potassium carbonate, 302.5; rubidium carbonate, 315.0 mg) are for more than the calculated weight losses (249.7, 245.4, 235.0 mg, respectively) required for the reaction:
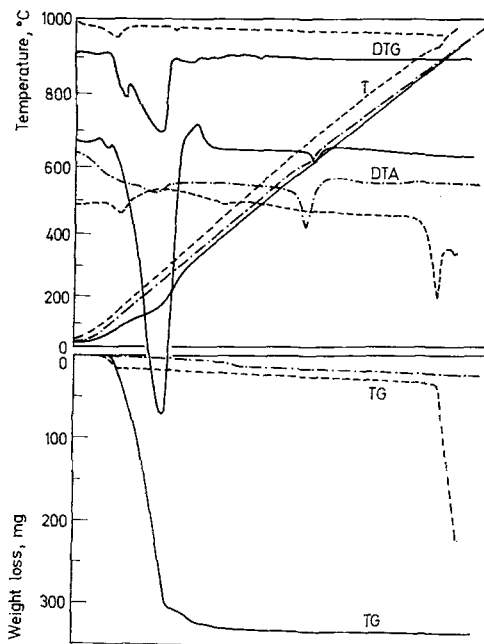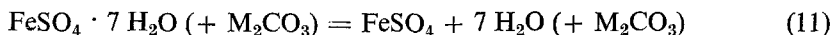
$$\text{FeSO}_4 \cdot 7\,\text{H}_2\text{O} \; (+\; \text{M}_2\text{CO}_3) = \text{FeSO}_4 + 7\,\text{H}_2\text{O} \; (+\; \text{M}_2\text{CO}_3) \qquad (11)$$

Fig. 3. Thermal decomposition of $\text{FeSO}_4 \cdot 7\,\text{H}_2\text{O}$ in air in the presence of K_2CO_3. ——— $\text{FeSO}_4 \cdot 7\,\text{H}_2\text{O} + \text{K}_2\text{CO}_3$; ------ K_2CO_3; —·—·—·— K_2SO_4. Weight of mixture: 836.6 mg; weight of sulphate: 541.41 mg; weight of carbonate: 295.19 mg

It is therefore suggested that part of the heptahydrate reacts with the carbonate in question to form iron(II) carbonate, which in turn decomposes in the presence of moisture present to iron(II) hydroxide as per equations (3) and (5).

The third region of interest is that between 200 and 300° in the case of lithium carbonate, and 200 and 400° in the case of the other carbonates. The weight losses observed in these regions could not be accounted for by any specific reaction. The products of decomposition in this region contained considerable amounts of magnetic oxide (Fe_3O_4) and metal sulphate. The formation of a dark-green compound was observed in this region in the case of decomposition in the presence of sodium, potassium or rubidium carbonates. It is therefore suggested that the thermal decomposition in the presence of lithium carbonate (where no green compound
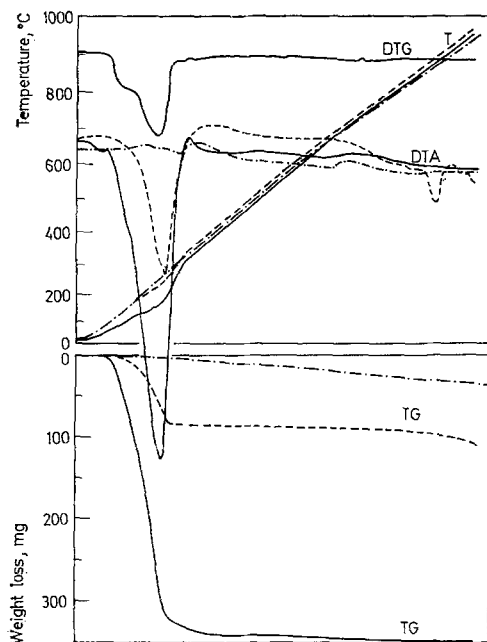
Fig. 4. Thermal decomposition of $FeSO_4 \cdot 7 H_2O$ in air in the presence of Rb_2CO_3. ———
$FeSO_4 \cdot 7 H_2O + Rb_2CO_3$; ------ Rb_2CO_3; — · — · — · — Rb_2SO_4; Weight of mixture: 986.45 mg; weight of sulphate: 517.31 mg; weight of carbonate: 469.14 mg

was observed) takes place via iron(II) carbonate and magnetic oxide, as represented by equations (3), (4), (7) and/or (8). In the case of the other carbonates, where the formation of a green compound was observed, the reaction takes place via equations (3), (5), (6), (7) and/or (8). The formation of iron(II) hydroxide by reaction (5) explains the observation of a green compound in this region. The exothermic reactions represented by equations (7) and (8), however, could not be detected in the DTA curve because of the simultaneous nature of the decomposition and oxidation reactions. The oxidation of the magnetic oxide, however, is represented by an exothermic peak $(320-440°)$ after the broad endothermic peak. Thus, the dehydration, oxidation and decomposition reactions of the heptahydrate in the presence of alkali metal carbonates are complete by about 450°, so that the overall reaction is represented by:

$$2 FeSO_4 \cdot 7 H_2O + 2 M_2CO_3 + \frac{1}{2} O_2 =$$
$$= Fe_2O_3 + 2 M_2SO_4 + 2 CO_2 + 14 H_2O. \tag{12}$$
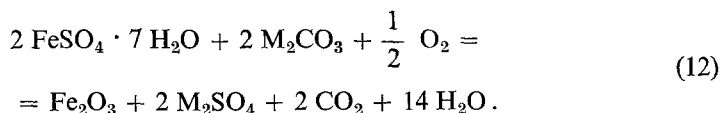
The calculated weight losses (lithium carbonate, 409.0, sodium carbonate, 321.0, potassium carbonate, 316.0, and rubidium carbonate, 302.0 mg) agree well with the observed weight losses (415.0, 325.0, 328.0 and 308.0 mg, respectively) (the

rubidium carbonate contains about 6% moisture and the potassium carbonate about 0.8% moisture, which must be taken into account).

The DTA curve for the decomposition of the heptahydrate in the presence of lithium carbonate shows two endothermic peaks, at 630 and 910°. Examination of the curve for lithium sulphate (Fig. 1) shows that the peak at 630° is due to the crystal transformation of lithium sulphate, and that at 930° is due to its melting. Similarly, a broad endothermic peak occurs in the region 880—940° in the case of decomposition in the presence of sodium carbonate (Fig. 2). This is attributed to the combined melting of sodium carbonate (900°) and sodium sulphate (940°). The peak at 630° in the case of decomposition in the presence of potassium carbonate is attributed to the crystal transformation of potassium sulphate (Fig. 3). X-ray diffraction data on the final products of decomposition showed the following:

System	Products
Iron(II) sulphate + lithium carbonate	Alpha and gamma-iron(III) oxides, lithium sulphate and small amounts of lithium ferrite and carbonate.
Iron(II) sulphate + sodium carbonate	Alpha-iron(III) oxide, sodium sulphate and small amounts of sodium ferrite.
Iron(II) sulphate + potassium carbonate	Alpha-iron(III) oxide, potassium sulphate and small amounts of potassium ferrite.
Iron(II) sulphate* + rubidium carbonate	Alpha-iron(III) oxide, rubidium sulphate and rubidium carbonate.

* Iron(II) sulphate heptahydrate.

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References

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2. idem., ibid., 16 (1979) 471.
3. M. S. R. SWAMY and T. P. PRASAD, J. Thermal Anal., 19 (1980) 297.
4. N. SH. SAFIULLIN, E. B. GITIS and N. M. PANASENKO, J. Appl. Chem. U.S.S.R., 42 (1969) 1843.

ZUSAMMENFASSUNG — Die thermische Zersetzung von Eisen(II)-sulfat-Heptahydrat wurde in Luft unter dynamischen Bedingungen in Gegenwart von Lithium-, Natrium-, Kalium und Rubidiumcarbonat ausgeführt. In Gegenwart von Lithiumcarbonat verläuft die Zersetzung auf einem anderen Wege als in Gegenwart der anderen untersuchten Carbonate. In Gegenwart von Lithiumcarbonat verliert das Heptahydrat alle Wassermoleküle, bevor es mit dem Car-

bonat in Reaktion tritt. Das wasserfreie Sulfat reagiert mit dem Carbonat vermutlich unter Bildung von Eisen(II)-carbonat, das oxydativ über Magnetit zu Eisen(III)-oxid zersetzt wird. Im Falle der anderen Carbonate tritt Eisen(II)-sulfat mit dem betreffenden Carbonat noch vor der völligen Beendigung der Dehydratation unter Bildung von Eisen(II)-carbonat in Reaktion, das daraufhin mit noch vorhandenem Wasser zu grünem Eisen(II)-hydroxid weiterreagiert. Diese Verbindung zersetzt sich oxydativ über Magnetit zu Eisen(III)-oxid

Резюме — В динамических условиях и в атмосфере воздуха проведено термическое разложение гептагидрата сульфата двухвалентного железа в присутствии карбонатов лития, натрия, калия и рубидия. Разложение сульфата в присутствии карбоната лития отличается от разложения в присутствии других карбонатов. В присутствии карбоната лития гептагидрат теряет все молекулы воды перед тем как вступить в реакцию с карбонатом. Безводный сульфат затем реагирует с карбонатом, образуя главным образом карбонат двухвалентного железа, который подвергается дальнейшему окислительно-восстановительному разложению до окиси трехвалентного железа через промежуточную стадию образования магнитной окиси железа. При наличии других карбонатов сульфат двухвалентного железа перед дегидратацией вступает в реакцию с карбонатом, образуя карбонат двухвалентного железа, который затем реагирует с находящейся там влагой с образованием зеленой гидроокиси двухвалентного железа. Это соединение подвергается реакции разложения — окисления через промежуточную стадию образования магнитной окиси железа до конечного продукта окиси трехвалентного железа.