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THERMAL DECOMPOSITION OF IRON(II) SULPHATE HEPTAHYDRATE IN AIR IN THE PRESENCE OF BASIC MAGNESIUM CARBONATE

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Results on the thermal decomposition of iron(II) sulphate heptahydrate in the presence of basic magnesium carbonate are presented and discussed. These results are compared with those for the mixture of iron(II) sulphate heptahydrate with basic beryllium carbonate. While no reaction occurs between the components in the case of basic beryllium carbonate, basic magnesium carbonate reacts readily with iron(II) sulphate heptahydrate.

In a previous communication [1], results on the thermal decomposition of iron(II) sulphate heptahydrate in the presence of basic beryllium cabonate were presented. It may be recalled that the components, iron(II) sulphate heptahydrate and basic beryllium carbonate, do not react at all under the dynamic oonditions studied, but undergo individual decompositions. Therefore, it was felt that it would be interesting to study the reaction of iron(II) sulphate heptahydrate with basic magnesium carbonate under the same conditions.

Experimental

Materials

Iron(II) sulphate heptahydrate was prepared and analysed as described earlier [2]. Basic magnesium carbonate, of composition $MgCO_3 \cdot 3Mg(OH)_2$, was prepared and analysed in the laboratory.

Apparatus and method

Thermal decomposition studies were made using the OD–102 derivatograph supplied by Metrimpex, Budapest, Hungary. The instrument records simultaneously and photographically differential thermal analysis (DTA), derivative

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thermogravimetric analysis (DTG), thermogravimetric (TG) and temperature (T) curves. In this investigation, the temperature of the sample was recorded. Cylindrical 'Platinel' crucibles were used. The sample mass was about 900 mg, with a matching amount of α-alumina as the reference material. The investigations were carried out from ambient temperature to 1000°, using the standard heating rate of 10 deg/min. Slight suction was applied to the furnace to remove any gases evolved from the sample.

A Philips PW 1051 X-ray diffractometer was used to study the intermediate phases as well as the final decomposition products.

To study the intermediates, the material under investigation was heated up to the temperature of interest in the normal way, then removed from the furnace of the thermobalance, cooled quickly and analysed immediately.

The kinetics of thermal decomposition were studied by the method used earlier [3]. The heats of decomposition were obtained from the areas under the DTA peaks by comparison with that for a standard material (e.g. sodium nitrate). The accuracy expected from such measurements is ± 10%.

Results and discussion

Figure 1 represents the thermal decomposition of iron(II) sulphate heptahydrate in the presence of basic magnesium carbonate. Curve (a) shows the thermal decomposition of the mixture, while curves (b) and (c) show the thermal decompositions of basic magnesium carbonate and magnesium sulphate, respectively.

The thermal decomposition of iron(II) sulphate heptahydrate in the presence of basic magnesium carbonate, may conveniently be dividdd into three major steps of weight loss. The weight loss data are presented in Table 1.

The first weight loss step, which includes the inflexion at 110°*, covers the range 70–200°, with an endothermic DTA peak at 180°. The observed and calculated weight losses can be accounted for by assuming the reaction:

$$\begin{aligned} &\mathrm{MgCO_3 \cdot 3Mg(OH)_2 + 3\,FeSO_4 \cdot 7H_2O} = \\ &= \underbrace{\mathrm{MgCO_3 + 3\,MgSO_4 + 3\,Fe(OH)_2}}_{\text{intermediate I}} + 21\,\mathrm{H_2O} \end{aligned} \qquad (1)$$

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* The inflextion at 110° does not represent any definite reaction in the system. As in the case of the thermal decomposition of pure $FeSO_4 \cdot 7H_2O$ [1], it only represents a change in the course of the reaction.

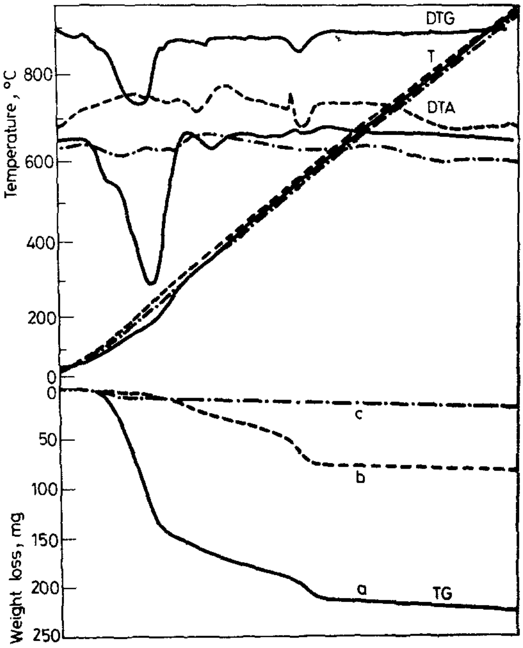

Fig. 1 TG, DTG and DTA curves of $FeSO_4 \cdot 7H_2O$ in the presence of basic magnesium carbonate. (a) $FeSO_4 \cdot 7H_2O + MgCO_3 \cdot 3Mg(OH)_2$ (·· —— —); (b) $MgCO_3 \cdot 3Mg(OH)_2$ (– – – –); (c) $MgSO_4$ (–.–.–.–.–)

Table 1 Thermal decomposition of $FeSO_4 \cdot 7H_2O$ in the presence of $MgCO_3 \cdot 3Mg(OH)_2$

Sl. No.	Temp. region, °C	Peak temp., °C	Wt. loss (%)		Probable reaction
			obsd.	calcd.	
1	70–200	180	34.10	34.59	1
2	200–520	360	7.50	7.30	2
3	520–560	540	6.40	6.43	3

Numbers 1, 2 and 3 correspond to reactions (1), (2) and (3) given in the text.

The material taken out at 200° was found to be non-magnetic and to give X-ray diffraction lines corresponding to $MgSO_4$ (d = 4.16, 3.53 and 3.61 Å) and $MgCO_3$ (d = 2.74, 2.10 and 1.70 Å). This supports the reaction represented by Eq. (1).

The second step covers the temperature interval 200–520°, with an endothermic DTA peak at 360°. The observed and calculated weight losses agree well for the decomposition of the intermediate I:

$$\begin{aligned} & MgCO_3 + 3\,MgSO_4 + 3\,Fe(OH)_2 + 3/4\,O_2 = \\ & = \underbrace{MgCO_3 + 3\,MgSO_4 + 3/2\,Fe_2O_3}_{\text{intermediate II}} + 3\,H_2O \end{aligned} \tag{2}$$

Thus, in effect Eq. (2) represents the oxidation of $Fe(OH)_2$ to Fe_2O_3, along with the loss of hydroxide water. The overall reaction is endothermic. The product taken out at 500° contained Fe_2O_3 (d = 2.69 and 3.66 Å) and $MgCO_3$ (d = 2.74, 2.10 and 1.70 Å), in support of the above reaction.

The third and final reaction step covers the temperature interval 520–560°, with an endothermic DTA peak at 540°. The observed and calculated weight losses agree well for the decomposition of the intermediate II:

$$MgCO_3 + 3\,MgSO_4 + 3/2\,Fe_2O_3 = MgO + 3\,MgSO_4 + 3/2\,Fe_2O_3 + CO_2 \tag{3}$$

Thus, this reaction is in effect the thermal decomposition of magnesium carbonate to magnesium oxide. This is also evident from the similarity of the TG curves for the mixture (curve (a) and for pure basic magnesium carbonate (curve (b)) in this temperature interval (Fig. 1).

The kinetics of thermal decomposition were evaluated only for the major reaction Eq. (1). The heat of the double decomposition reaction was calculated for the overall reaction involving other small peaks represented by Eqs (2) and (3). The overall reaction is:

$$\begin{aligned} & MgCO_3 \cdot 3Mg(OH)_2 + 3\,FeSO_4 \cdot 7H_2O + 3/4\,O_2 = \\ & = MgO + 3\,MgSO_4 + 3/2\,Fe_2O_3 + CO_2 + 24\,H_2O \end{aligned} \tag{4}$$

The results are given in Table 2.

Table 2 Some kinetic and thermochemical parameters

S. No.	Reaction	E, kJ/mole	Mech. Eq.	Model	ΔH, kJ/mole
1	$MgCO_3 \cdot 3Mg(OH)_2 + 3FeSO_4 \cdot 7H_2O$ $= MgCO_3 + 3MgSO_4 + 3Fe(OH)_2 + 21H_2O$	76.00	α^2	1*	—
2	$MgCO_3 \cdot 3Mg(OH)_2 + 3FeSO_4 \cdot 7H_2O +$ $3/4\,O_2$ $= MgO + 3MgSO_4 + 3/2\,Fe_2O3 + CO_2 +$ $+ 24\,H_2O$		+	+	428.4

* One dimensional diffusion with constant diffusion coefficient.

Table 3 X-ray diffraction data for the final product

Sl. No.	"d" value, Å	Relative intensity	Probable phase
1	4.16	30	$MgSO_4$
2	3.66	30	Fe_2O_3
3	3.61	30	$MgSO_4$
4	3.53	100	$MgSO_4$
5	3.36	10	$MgSO_4$
6	2.69	100	Fe_2O_3
7	2.50	30	Fe_2O_3
8	2.44	10	MgO
9	2.11	50	MgO
10	1.83	30	Fe_2O_3
11	1.68	30	Fe_2O_3
12	1.59	30	Fe_2O_3
13	1.49	50	MgO
14	1.45	10	Fe_2O_3

The X-ray diffraction data for the final product of decomposition (Table 3) show the presence of iron(II) oxide, magnesium sulphate and magnesium oxide.

From the results presented so far, it is evident that basic magnesium carbonate behaves in an entirely different way from basic baryllium carbonate. In view of this vast difference in behaviour between these two basic carbonates, investigations have also been carried out on the thermal decompositions of iron(II) sulphate heptahydrate in the presence of calcium, barium and strontium carbonates. The results will form the subject of a future communication.

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References

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Zusammenfassung — Bei der in Gegenwart von basischem Magnesiumcarbonat erfolgten thermischen Zersetzung von Eisen(II)-sulfat-Heptahydrat erhaltene Ergebnisse werden beschrieben, diskutiert und mit denen verglichen, die in Gegenwart von Berylliumcarbonat erhalten wurden. Im Gegensatz zu basischem Berylliumcarbonat reagiert basisches Magnesiumcarbonat mit Eisen(II)-sulfat-Heptahydrat.

Резюме — Представлены и обсуждены результаты термического разложения гептагидрата сульфата двухвалентного железа в присутствии основной соли карбоната магния. Полученные результаты сопоставлены с таковыми для основного карбоната бериллия. Установлено, что в то время как основной карбонат бериллия не вступает в реакцию, основной карбонат магния хорошо реагирует с гептагидратом сульфата двухвалентного железа.