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

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Iron(II) sulphate heptahydrate undergoes decomposition in the presence of basic beryllium carbonate without any interaction with the carbonate. The components of the mixture decompose individually. Iron(II) sulphate decomposes with the formation of tetrahydrate, monohydrate, anhydrous salt, oxysulphate and ferric sulphate as intermediate phases. The basic beryllium carbonate decomposes to the oxide with $BeO \cdot BeCO_3$ as the intermediate compound.

In a previous communication [1], we presented results on the thermal decomposition of iron(II) sulphate heptahydrate in air in the presence of alkali metal carbonates. Iron(II) sulphate heptahydrate reacts with these carbonates to give iron(III) oxide and alkali metal sulphate as major products, along with small amounts of metal ferrite. The reaction path involves intermediates such as iron(II) carbonate, iron(II) hydroxide and magnetic oxide of iron. In this communication we present results on the thermal decomposition of the heptahydrate in air in the presence of basic beryllium carbonate.

Experimental

Materials

Iron(II) sulphate heptahydrate was prepared and analysed as described earlier [1]. Beryllium carbonate was a product of E. Merck, "pure" grade, with a minimum assay of 99%. It has the formula $Be(OH)_2 \cdot BeCO_3$.

Apparatus and method

As in our previous communication [1].

Results and discussion

Figure 1 represents the thermal decomposition of the heptahydrate in the presence of beryllium carbonate. The individual decompositions of basic beryllium carbonate and beryllium sulphate are presented in the same Figure. The weight

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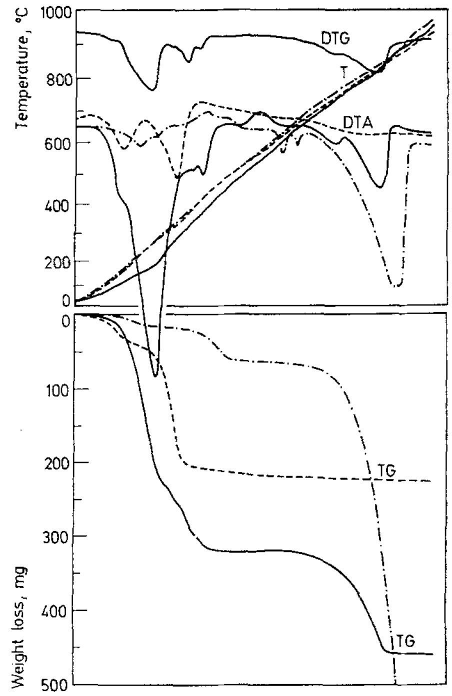

Fig. 1. Thermal decomposition of $FeSO_4 \cdot 7\,H_2O$ in the presence of $BeCO_3$. ——— $FeSO_4 \cdot 7\,H_2O + BeCO_3$; ------ $BeCO_3$; —·—·—·—. $BeSO_4$

loss data are presented in Table 1. It is evident from the Figure that basic beryllium carbonate undergoes decomposition in the same region as the heptahydrate [2]. The carbonate undergoes decomposition in two steps, the first being the removal of –OH as water and the second being the removal of the carbonate group as carbon dioxide. The first phase of decomposition occurs in the range 60–220°, where the heptahydrate is expected to lose six water molecules. Thus, the calculated weight loss for the loss of one molecule of water from the basic carbonate and six molecules of water from the heptahydrate agrees fairly well with the observed weight loss in this region (Table 1).

The intermediate compound, a mixture of $BeO \cdot BeCO_3$ and $FeSO_4 \cdot H_2O$, now undergoes decomposition, the former losing carbon dioxide and the latter losing the lone water molecule, to give a mixture of BeO and $FeSO_4$ as the new intermediate compound. These reactions take place in the region 220–480°. For convenience, the combined weight loss for the two steps was calculated. As can be seen from the Table, the agreement is good. It may be mentioned here that the second intermediate compound need not be simply a mixture of BeO and $FeSO_4$. As reported earlier [2], partial oxidation of iron(II) to iron(III) always takes place to-

Table 1

Thermal decomposition of iron(II) sulphate heptahydrate in the presence of basic beryllium carbonate

Amount of mixture taken = 663.28 mg;
heptahydrate content of mixture = 506.2 mg;
basic carbonate content of mixture = 157.08 mg

Serial No.	Probable reaction	Temp. range °C	Wt. change, mg	
			calcd.	obsed.
1.	$Be(OH)_2 \cdot BeCO_3 = BeO \cdot BeCO_3 + H_2O$ $FeSO_4 \cdot 7\,H_2O = FeSO_4 \cdot H_2O + 6\,H_2O$	60–220	−222	−223
2.	$Be(OH)_2 \cdot Be(CO_3) = 2\,BeO + H_2O + CO_2$ $FeSO_4 \cdot 7\,H_2O = FeSO_4 + 7\,H_2O$	60–480	−316.34	−318
3.	$2\,FeSO_4 + 1/2\,O_2 = Fe_2O(SO_4)_2$	500–600	+14.6	+10
4.	$Fe_2O(SO_4)_2 = Fe_2O_3 + 2\,SO_3$	600–880	−146	−143

gether with the loss of water molecules, and hence we expect some iron(III) compound (presumably the oxysulphate) in the intermediate compound.

Next, the iron(II) sulphate of the second intermediate is oxidized to the oxysulphate; the oxidation reaction is indicated by a weight gain in the TG curve and an exothermic peak (around 560°) in the DTA curve. The calculated and observed weight gains do not agree (Table 1), because of the partial oxidation mentioned above. The intermediate compound now consists of BeO and $Fe_2O(SO_4)_2$.

The region 600–880° involves the decomposition of the oxysulphate. The DTA curve shows two endothermic peaks, at 750° and 850°. It has been pointed out earlier [2, 3] that the oxysulphate may undergo decomposition simultaneously by two paths: one direct decomposition to the oxide, and the other via iron(III) sulphate to the oxide:

$$Fe_2O(SO_4)_2 = Fe_2O_3 + 2\,SO_3 \tag{1}$$

$$\begin{aligned} 3\,Fe_2O(SO_4)_2 &= Fe_2O_3 + 2\,Fe_2(SO_4)_3 \\ 2\,Fe_2(SO_4)_3 &= 2\,Fe_2O_3 + 6\,SO_3 \end{aligned} \tag{2}$$

The first reaction corresponds to the peak at 750°, and the second reaction (decomposition of iron(III) sulphate) to the second peak. The overall reaction in the region 600–880° thus amounts to the decomposition of the oxysulphate to iron(III) oxide and sulphur trioxide as represented by equation 1. From the Table it can be seen that the calculated and the observed weight losses agree quite well.

Thus, the overall reaction between the heptahydrate and basic beryllium carbonate in the region 60–880° can be represented as:

$$\begin{aligned} &2\,FeSO_4 \cdot 7\,H_2O + 2\,Be(OH)_2 \cdot BeCO_3 + \tfrac{1}{2}\,O_2 = \\ &Fe_2O_3 + 4\,BeO + 2\,CO_2 + 2\,SO_3 + 16\,H_2O \end{aligned} \tag{3}$$

The calculated (447.4 mg) and the observed (450 mg) weight losses agree quite well.

Samples withdrawn in the region 500–600° contained oxysulphate and beryllium oxide. No evidence (X-ray) for the presence of beryllium sulphate could be obtained at any stage of the decomposition. Further, the absence of the two endothermic peaks at 640 and 680°, characteristic of beryllium sulphate, confirms the nonformation of beryllium sulphate. The final product contained alpha-iron(III) oxide and beryllium oxide.

There is no inflexion point in the decomposition curve of basic beryllium carbonate around 110°. The inflexion at 110° in the DTA curve of the mixture may therefore be taken as due to the formation of the tetrahydrate, on analogy with the pure heptahydrate [4].

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Zusammenfassung — In Gegenwart von basischem Berylliumcarbonat zersetzt sich Eisen(II)-sulfat-Heptahydrat, ohne mit dem Carbonat in Wechselwirkung zu treten. Die Komponenten des Gemisches zersetzen sich individuell. Die Zersetzung des Eisen(II)-sulfats verläuft über die Zwischenphasen Tetrahydrat, Monohydrat, wasserfreies Salz, Oxysulfat und Eisen(III)-sulfat. Das basische Berylliumcarbonat wird über die intermediäre Verbindung BeO · $BeCO_3$ in das Oxid überführt.

Резюме — Гептагидрат сульфата двухвалентного железа подвергается разложению в присутствии основного карбоната бериллия, вступая с ним в реакцию. Компоненты полученной при этом смеси разлагаются индивидуально. Сульфат двухвалентного железа разлагается с образованием тетрагидрата, моногидрата, безводной соли, оксисульфата и сульфата трехвалентного железа как промежуточных продуктов. Основной карбонат бериллия разлагается до окиси с образованием промежуточного продукта $BeO.BeCO_3$.