

## SOLID-STATE REACTIONS BETWEEN ALKALI PERSULFATES AND OXIDES OF CORUNDUM STRUCTURE

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### ABSTRACT

The effects of three corundum structure oxides,  $\alpha\text{-Al}_2\text{O}_3$ ,  $\alpha\text{-Cr}_2\text{O}_3$ , and  $\alpha\text{-Fe}_2\text{O}_3$ , on the thermal decomposition of sodium and potassium peroxodisulfates (persulfates) under non-isothermal static air conditions and using various oxide/persulfate molar ratios, have been thermoanalytically investigated. Compounds such as  $\text{Na}_3\text{Al}(\text{SO}_4)_3$ ,  $\text{K}_3\text{Al}(\text{SO}_4)_3$ ,  $\text{Cr}_2(\text{SO}_4)_3$ ,  $\text{K}_3\text{Cr}(\text{SO}_4)_3$ , and  $\text{Na}_3\text{Fe}(\text{SO}_4)_3$  are identified by X-ray diffractometry and conventional chemical analysis. The molar ratios as well as temperatures of the stoichiometric formation for these compounds have been established. At higher temperatures,  $\alpha\text{-Al}_2\text{O}_3$  acts as a promoter catalyst for the decomposition of pyrosulfate to sulfate, whereas  $\alpha\text{-Cr}_2\text{O}_3$  behaves as a retarder for the decomposition of persulfate. A eutectic mixture is formed between  $\text{K}_3\text{Al}(\text{SO}_4)_3$  and  $\text{K}_2\text{SO}_4$  at  $675^\circ\text{C}$ . Also,  $\text{K}_3\text{Fe}(\text{SO}_4)_3$  is identified as two crystalline phases.

### INTRODUCTION

The three oxides,  $\alpha\text{-Al}_2\text{O}_3$ ,  $\alpha\text{-Cr}_2\text{O}_3$  and  $\alpha\text{-Fe}_2\text{O}_3$ , belong to the corundum structure [1] in that they have rhombohedral hexagonally close-packed ionic crystals [2,3]. It is worth mentioning that the defect in the lattice structure is so small that no adequate analytical technique is available for its measurement [4]. Moreover, the *p*-type semiconductivity of  $\alpha\text{-Cr}_2\text{O}_3$  increases with the rise in number of defective sites of its lattice structure. Nevertheless, the oxide behaves as an electric conductor when heated to high temperatures [4]. Further, the semiconductive behavior of  $\alpha\text{-Fe}_2\text{O}_3$  is due to a defective lattice structure caused by the deficiency of oxygen atoms on both sides of the  $\text{Fe}^{3+}$  ion. Because of the presence of some impurities, iron(III) oxide may behave as a *p*- or *n*-type semiconductor. The catalytic effects of some oxides, including those mentioned above, on the thermal decomposition of the chlorate and perchlorate of potassium, as well as other salts, were studied [5–14].

Jasim and co-workers [15–24] studied high temperature reactions of binary systems of transition metals and lanthanide oxides with persulfates of sodium and potassium and found interesting results.

In this work we have studied the thermal reactions of six oxide—persulfate

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binary systems to establish the proper conditions for optimal catalysis, compound formation, phase transition, and thermal stabilities of intermediate and final products.

## EXPERIMENTAL

Reagents, preparation of samples, thermal and X-ray diffraction analyses equipment were as described previously [20].

## RESULTS AND DISCUSSION

### *Aluminium(III) oxide—persulfate systems*

Figures 1 and 2 show the derivatograms of  $\alpha\text{-Al}_2\text{O}_3\text{--Na}_2/\text{K}_2\text{S}_2\text{O}_8$  for the molar ratios 1 : 6, 1 : 3, 1 : 2, 2 : 3, 1 : 1, and 4 : 3. Neither the TG nor the DTA curves indicate any significant effect of  $\alpha\text{-Al}_2\text{O}_3$  on the  $T_i$  and  $T_f$  of decomposition of sodium or potassium persulfate into pyrosulfate.

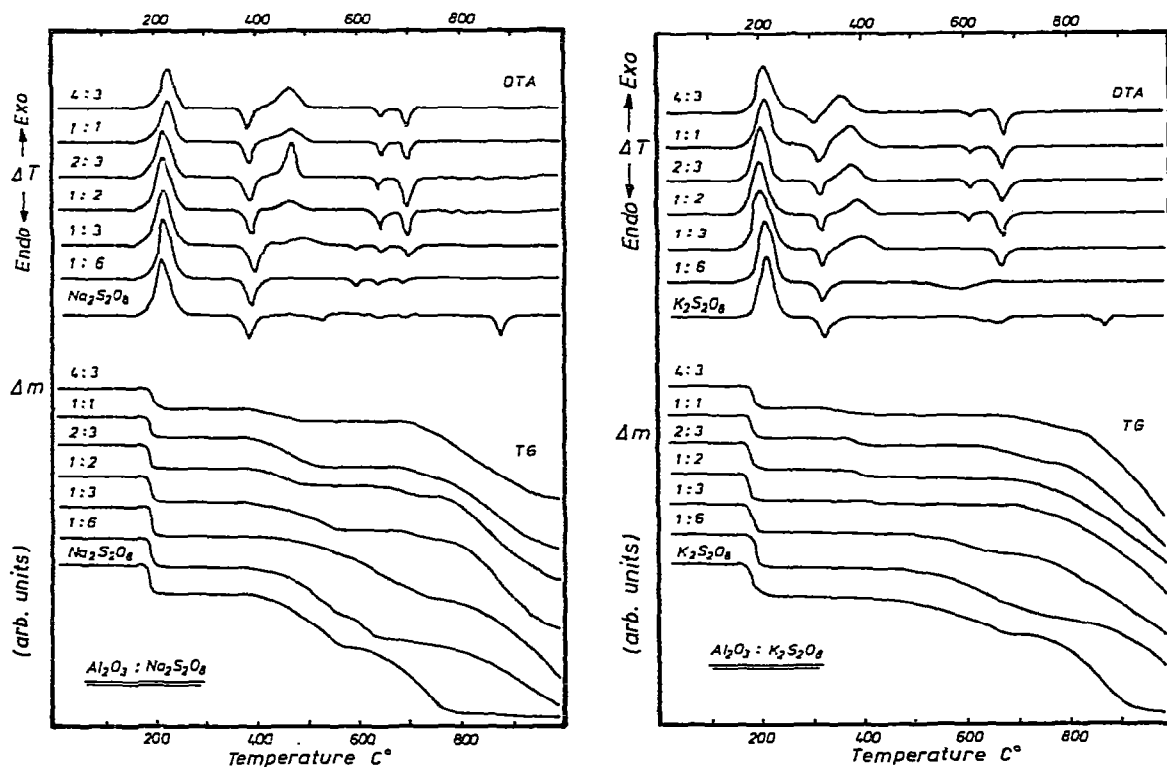
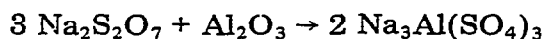


Fig. 1. TG and DTA curves of aluminium(III) oxide—sodium persulfate mixtures.

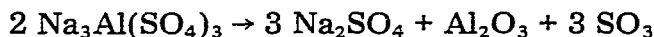
Fig. 2. TG and DTA curves of aluminium(III) oxide—potassium persulfate mixtures.

$\alpha\text{-Al}_2\text{O}_3\text{--Na}_2\text{S}_2\text{O}_8$  system

The TG curves (Fig. 1) reveal that part of the thermally produced  $\text{Na}_2\text{S}_2\text{O}_7$  undergoes thermal decomposition before reacting with  $\alpha\text{-Al}_2\text{O}_3$ . Calculation proved that the loss in weight is proportional to the amount of persulfate already present in the mixture, except for the molar ratios 1 : 1 and 4 : 3, where the loss is not proportional (Table 1). Also, a horizontal plateau is seen on the TG curve of the stoichiometric ratio 2 : 3 between 510 and 670°C. Samples isolated at 520°C gave XRD patterns [ $d$ -lines (Å) = 3.12, 3.00, 3.93] which indicate the presence of relatively large amounts of  $\text{Na}_3\text{Al}(\text{SO}_4)_3$  as well as traces of  $\text{Na}_2\text{SO}_4$  and  $\alpha\text{-Al}_2\text{O}_3$ . In the meantime, the DTA curves did not exhibit any change in the melting point of the pure  $\text{Na}_2\text{S}_2\text{O}_7$  produced in the presence of the oxide, but after melting the  $T_i$  of  $\text{Na}_2\text{S}_2\text{O}_7$  immediately lowers as the oxide content increases in the mixture. The stoichiometric equation for this reaction is



The presence of a little sodium sulfate, as traced by X-ray diffraction analysis, is due to the fact that some of the  $\text{Na}_2\text{S}_2\text{O}_7$  decomposes before reacting with the oxide. However, the TG curve for the 2 : 3 ratio registers a weight loss of 4.5% between 670 and 700°C; the curve then levels off until 770°C. Samples sintered at 740°C when examined by X-ray diffractometry proved to be mainly  $\text{Na}_3\text{Al}(\text{SO}_4)_3$ , from which it can be safely deduced that this weight loss is attributed to a partial decomposition of this salt



This leads to the conclusion that the decomposition of the salt formed at the 2 : 3 ratio occurs in two consecutive stages, whereas in the 1 : 1 and 1 : 2 ratios the salt decomposes in one step only due to the presence of excess  $\alpha\text{-Al}_2\text{O}_3$  which accelerates its decomposition through catalysis.

The three endotherms observed on the DTA curve of the 1 : 6 ratio between 580° and 710°C is ascribable to thermal decomposition of  $\text{Na}_2\text{S}_2\text{O}_7$  only. The first endo peak seen on the curves of the other ratios at 640°C concerns the melting point of impure pyrosulfate [16,25]; that at 695°C is the melting point of  $\text{Na}_3\text{Al}(\text{SO}_4)_3$ , which differs by 20°C from values found by Fedorov and Chang [25]. This difference is perhaps because we used the Paulik—Erdy method for estimating the melting point of the salt.

$\alpha\text{-Al}_2\text{O}_3\text{--K}_2\text{S}_2\text{O}_8$  system

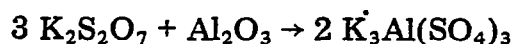
From calculations of the thermoanalytical curves (Fig. 2), it is shown that the reaction between the thermally produced pyrosulfate and  $\alpha\text{-Al}_2\text{O}_3$  is shifted to a lower temperature value as the oxide content increases, and reaches 320°C with the ratio 4 : 3. A small percent (1.5—4.5) of  $\text{K}_2\text{S}_2\text{O}_7$  has been decomposed at this temperature. This is because the pyrosulfate starts decomposition after melting by an interval of 50°C [15], whence it has sufficient time to react with the oxide [18]. In the 1 : 2 stoichiometric ratio

TABLE 1

Accumulated data from thermoanalytical investigations of the six binary systems of the proper stoichiometric ratios, and XRD patterns of compounds obtained

| Binary systems                                                                          | Ratio | O <sub>2</sub> lost<br>(mg) |       | Persulfate<br>decomp.<br>temp. (°C) | Reaction<br>temp, T <sub>i</sub><br>(°C) | Formula of<br>compound<br>formed                  | Thermal<br>stability<br>(°C) | XRD patterns<br>d(Å) |
|-----------------------------------------------------------------------------------------|-------|-----------------------------|-------|-------------------------------------|------------------------------------------|---------------------------------------------------|------------------------------|----------------------|
|                                                                                         |       | Calc.                       | Found |                                     |                                          |                                                   |                              |                      |
| $\alpha$ -Al <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> | 2 : 3 | 12.8                        | 12.5  | 190                                 | 235                                      | Na <sub>3</sub> Al(SO <sub>4</sub> ) <sub>3</sub> | 510-770                      | 3.12, 3.00, 3.93     |
| $\alpha$ -Al <sub>2</sub> O <sub>3</sub> -K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>  | 1 : 2 | 11.83                       | 11.5  | 185                                 | 225                                      | K <sub>3</sub> Al(SO <sub>4</sub> ) <sub>3</sub>  | 335-675                      | 3.25, 2.75, 7.45     |
| $\alpha$ -Cr <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> | 1 : 3 | 11.08                       | 11.00 | 158                                 | 230                                      | Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>   | 350-670                      | 5.92, 3.55, 2.751    |
| $\alpha$ -Cr <sub>2</sub> O <sub>3</sub> -K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>  | 1 : 3 | 9.96                        | 10.0  | 167                                 | 225                                      | K <sub>3</sub> Cr(SO <sub>4</sub> ) <sub>3</sub>  | 330-760                      | 3.24, 7.41, 2.76     |
| $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> | 1 : 3 | 10.98                       | 10.50 | 198                                 | 235                                      | Na <sub>3</sub> Fe(SO <sub>4</sub> ) <sub>3</sub> | 385-665                      | 3.19, 6.80, 3.04     |
| $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> -K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>  | 1 : 3 | 9.76                        | 9.0   | 160                                 | 200                                      | K <sub>3</sub> Fe(SO <sub>4</sub> ) <sub>3</sub>  | 280-700                      | 3.30, 7.41, 2.78     |

the system  $\alpha\text{-Al}_2\text{O}_3\text{--K}_2\text{S}_2\text{O}_8$  reacts to form  $\text{K}_3\text{Al}(\text{SO}_4)_3$



which is made obvious by the X-ray powder diffraction method (Table 1). As for samples sintered at  $570^\circ\text{C}$ , the XRD pattern also shows  $d(\text{\AA})$  lines for trace amounts of  $\text{K}_2\text{SO}_4$  (2.90, 3.00, 2.87), and  $\alpha\text{-Al}_2\text{O}_3$  (2.07, 1.61, 3.47).

It becomes evident from calculation of the  $\text{SO}_3$  gas liberated and X-ray analysis that potassium aluminium trisulfate decomposes slowly and continuously after melting up to the ceiling temperature of the heating program ( $1050^\circ\text{C}$ )



The sharp endotherm obtained at  $675^\circ\text{C}$  is evidently attributed to the formation of a eutectic of this salt with the potassium sulfate produced [26].

### *Chromium(III) oxide—persulfate systems*

Figures 3 and 4 show the DTA and TG curves, under static air atmosphere of various molar ratios of  $\text{Cr}_2\text{O}_3\text{--M}_2\text{S}_2\text{O}_8$  systems, where M is either Na or K. Contrary to the above-mentioned systems, the decomposition of the persulfate occurs in two steps represented as two large exotherms in the DTA

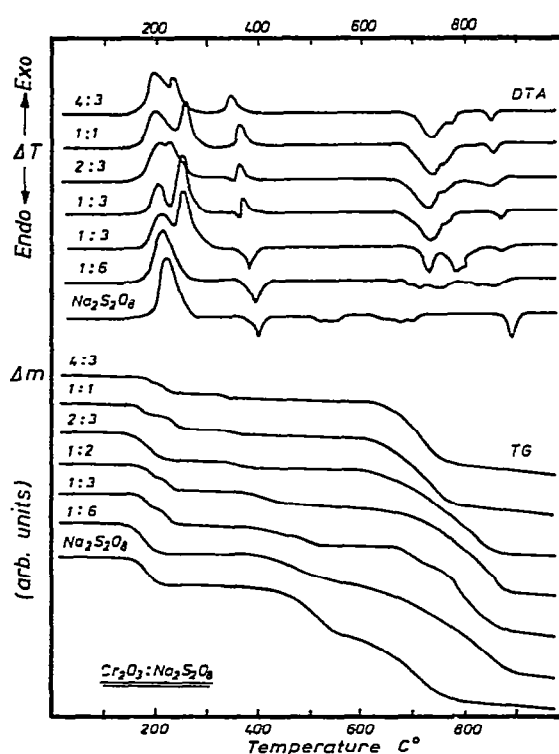


Fig. 3. TG and DTA curves of chromium(III) oxide—sodium persulfate mixtures.

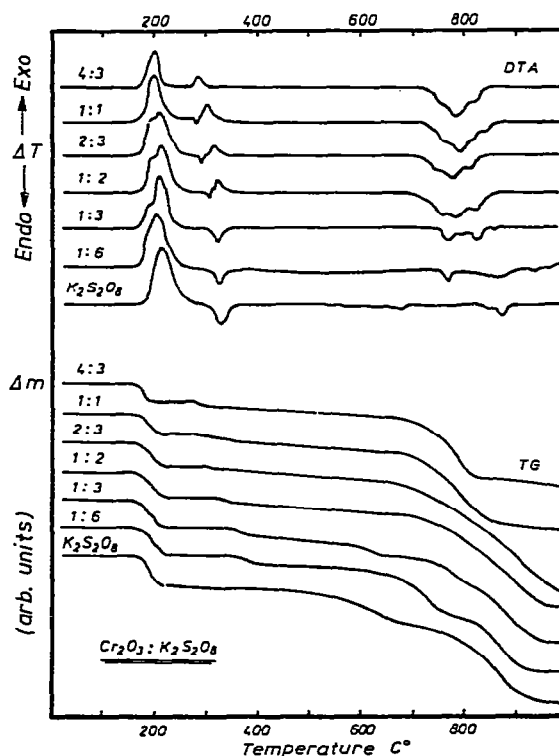
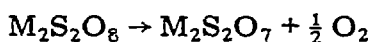
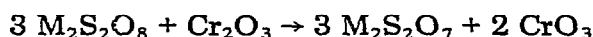


Fig. 4. TG and DTA curves of chromium(III) oxide—potassium persulfate mixtures.

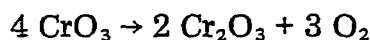
curves of Fig. 3, and as relatively small ones in DTA of Fig. 4. Also, the  $T_i$  values of the pure sodium or potassium persulfate decomposition were lowered and found to be 158 and 167°C, respectively. Since the two exotherms were not temperature resolved, it was rather difficult to sinter intermediates that give XRD patterns of known constitutions. However, the first exotherm could, perhaps, be ascribed to the partial decomposition of persulfate into pyrosulfate



as well as to a redox reaction



Thus the second exotherm may be imputed to thermal degradation of  $\text{CrO}_3$  into  $\text{Cr}_2\text{O}_3$  and oxygen atoms, and the latter combine through a secondary exothermic reaction [27–30]

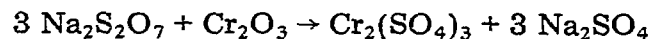


Further calculations indicate that the  $\text{O}_2$  liberated is equivalent to that obtained from direct decomposition of equal amounts of pure persulfate.

#### *$\text{Cr}_2\text{O}_3$ — $\text{Na}_2\text{S}_2\text{O}_8$ system*

Figure 3 shows that the melting point temperature of the thermally produced  $\text{Na}_2\text{S}_2\text{O}_7$  is lowered to 348°C in the 2 : 3 ratio. The two peaks that appear on DTA curves at 338 and 350°C for the 1 : 1 and 4 : 3 ratios, respectively, suggest that the reaction proceeds before or during the melting of pyrosulfate. Here the  $T_i$  is lowered as the ratio increases and approaches a minimum at 338°C in the 4 : 3 ratio.

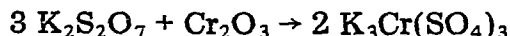
Further, the TG curves point out that part of the sodium pyrosulfate dissociates before reacting with the oxide. Thereafter, the reaction continues and the curves level off until  $\text{Cr}_2(\text{SO}_4)_3$  formation stops. It is to be observed that the  $T_i$ — $T_f$  of the reaction increases as the oxide content of the mixtures increases. On the other hand, X-ray analysis indicates that samples sintered at 620°C for the stoichiometric 1 : 3 molar ratio confirms the presence of  $\text{Cr}_2(\text{SO}_4)_3$ ,  $\text{Na}_2\text{SO}_4$ , and a little  $\text{Cr}_2\text{O}_3$ . Computed data reveal that other ratios could not give relatively as high a percent yield of  $\text{Cr}_2(\text{SO}_4)_3$ , whence the stoichiometric reaction can be written as follows



Furthermore, XRD patterns (Table 1) for samples of various molar ratios heated at temperatures between 670 and 880°C suggest that the chromium(III) sulfate dissociates into  $\text{Cr}_2\text{O}_3$  and  $\text{SO}_3$  gas. It is to be observed from Fig. 3 that  $T_i$ — $T_f$  values for this reaction are depressed by increasing the oxide proportion in samples. Moreover, the endo peak at the 1 : 6 ratio looks rather peculiar due to overlapping decomposition endotherms of  $\text{Cr}_2(\text{SO}_4)_3$  and excess  $\text{Na}_2\text{S}_2\text{O}_7$ , whereas in the 1 : 3 ratio its decomposition proceeds in three neighboring steps, and in other ratios it occurs in two steps only [31]. It is worth noting that the presence of  $\text{Cr}_2(\text{SO}_4)_3$  and  $\text{Cr}_2\text{O}_3$  lowers the melting point of the 2 : 3 ratio to a minimum of 845°C.

### *Cr<sub>2</sub>O<sub>3</sub>—K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system*

An exo peak is perceived on the DTA curves (Fig. 4) for the ratios 1 : 2, 2 : 3, 1 : 1, and 4 : 3, which is attributable to the exothermic reaction between K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> and Cr<sub>2</sub>O<sub>3</sub>. Also, the  $T_i$  of the reacting system decreases when the oxide proportion increases. This exo peak disappears in the stoichiometric ratio of 1 : 3 due to the thermal neutrality [19]. Samples of this ratio heated at 700°C gave an XRD pattern (Table 1) which indicates the formation of K<sub>3</sub>Cr(SO<sub>4</sub>)<sub>3</sub> as well as traces of Cr<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>SO<sub>4</sub>



Also the  $T_i$  for the decomposition of this salt decreases as the ratio becomes greater, such as the 4 : 3 ratio where it is lowered to 685°C. Conversely, the  $T_f$  becomes higher and arrives at 995°C for the 2 : 3 ratio; at higher molar ratios, e.g. 4 : 3, it reaches 820°C. This behavior could be accounted for by the continuous formation of the potassium chromium trisulfate up to the 2 : 3 ratio with evolution of excessive amounts of heat, while in the 4 : 3 ratio the oxide increases and catalytically decomposes the salt; a reaction which absorbs heat depresses  $T_f$ .

Moreover, the multistage thermal decomposition of K<sub>3</sub>Cr(SO<sub>4</sub>)<sub>3</sub> is shown as a corrugated broad endotherm on the DTA curves. No explanation could be offered as to why its decomposition occurs in such small steps and not suddenly. This endotherm also shows that the greater the oxide present in the mixture, the shorter the interval of  $T_i$ — $T_f$ .

However, samples heated at 1000°C for the various molar ratios give bright *d*-lines for Cr<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>SO<sub>4</sub> mainly due to thermal degradation of the trisulfate



### *Iron(III)oxide—persulfate systems*

The thermoanalytical curves of various molar ratios of oxide—persulfate systems are seen in Figs. 5 and 6. It is to be noted that the  $T_i$  for persulfate decomposition increases as the oxide—persulfate ratio becomes larger; a fact that is ascribed to the dilution effect of the oxide [19,32,33].

### *Fe<sub>2</sub>O<sub>3</sub>—Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system*

Figure 5 shows two exo peaks at 370 and 360°C for the ratios 2 : 3 and 4 : 3, respectively, indicating that their reactions occur before or during the melting of Na<sub>2</sub>S<sub>2</sub>O<sub>7</sub>, where a part of the evolved heat of a reaction is absorbed by the endothermic decomposition of the pyrosulfate. It is also found that the  $T_i$  of the reactions of the two ratios is lowered by raising their oxide content. This may happen by catalytic action of excess oxide; however, calculation using the TG curves proves that the amount of Na<sub>2</sub>S<sub>2</sub>O<sub>7</sub> decomposed, before reacting with the oxide, is proportional to the persulfate content of the sample.

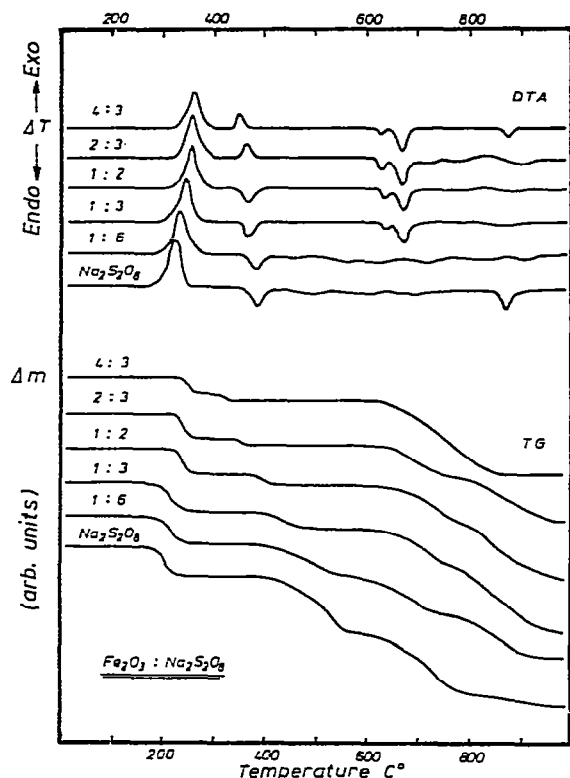


Fig. 5. TG and DTA curves of iron(III) oxide—sodium persulfate mixtures.

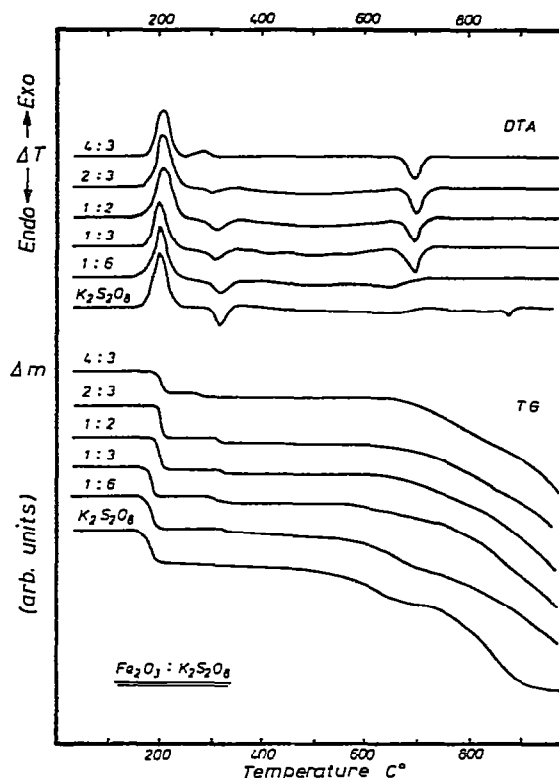
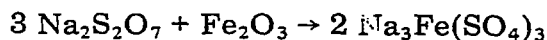


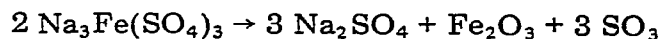
Fig. 6. TG and DTA curves of iron(III) oxide—potassium persulfate mixtures.

X-Ray powder analysis (Table 1) for samples heated at 620°C for the stoichiometric 1 : 3 ratio confirmed that  $\text{Na}_3\text{Fe}(\text{SO}_4)_3$  constitutes a major part of the intermediate products. The trace amounts of  $\text{Fe}_2\text{O}_3$  and  $\text{Na}_2\text{SO}_4$  are due, respectively, to excess oxide present and the decomposition of unreacted pyrosulfate. Evidently there is the stoichiometric reaction



The same compound was recognized when samples of 2 : 3 and 4 : 3 ratios were heated at 520 and 530°C, respectively. Here the  $d$ -lines for  $\text{Na}_2\text{SO}_4$  and  $\text{Fe}_2\text{O}_3$  are brighter than those obtained in the case of the 1 : 3 ratio, which suggests a relatively lower yield of  $\text{Na}_3\text{Fe}(\text{SO}_4)_3$ .

The sodium iron trisulfate starts decomposition at 665°C



For greater molar ratios such as 4 : 3, the  $T_i$ — $T_f$  for decomposition is rather squeezed where  $T_f$  approaches 865°C.

Careful observation of the DTA curves of the 1 : 3, 1 : 2, 2 : 3, and 4 : 3 ratios indicates two adjacent endotherms. That at 617°C belongs to the phase change of  $\text{Na}_3\text{Fe}(\text{SO}_4)_3$ , and the one at 665°C is a phase change due to melting and subsequent decomposition of the compound. Moreover, the area



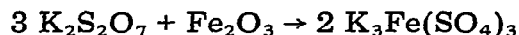
of the former endotherm reaches a maximum at the 2 : 3 ratio where the relative quantity of the salt is optimum.

For the 4 : 3 ratio the melting endotherm of  $\text{Na}_2\text{SO}_4$  becomes clearest at  $880^\circ\text{C}$ . This is because the thermal decomposition of  $\text{Na}_3\text{Fe}(\text{SO}_4)_3$ ,  $665\text{--}865^\circ\text{C}$ , takes place before the melting of the former.

#### *$\text{Fe}_2\text{O}_3\text{--K}_2\text{S}_2\text{O}_8$ system*

The melting point of  $\text{K}_2\text{S}_2\text{O}_7$  is lowered as the ratios increase and is found to be  $320$ ,  $316$ ,  $310$ , and  $300^\circ\text{C}$  for the ratios 1 : 6, 1 : 3, 1 : 2 and 2 : 3, respectively.

The exotherm at  $280^\circ\text{C}$  indicates that the reaction between the oxide and  $\text{K}_2\text{S}_2\text{O}_7$  happens before or during the melting of the latter. Samples heated at  $515$ ,  $600$ , and  $680^\circ\text{C}$  for the 1 : 3 ratio gave sharp *d*-lines (Table 1), identifying the presence of  $\text{K}_3\text{Fe}(\text{SO}_4)_3$  [34]



in addition to a little  $\text{K}_2\text{SO}_4$ .

Other sharp *d*-lines ( $3.26$ ,  $2.76$ ,  $2.81 \text{ \AA}$ ) of unknown identity (they have no counterpart in the ASTM cards) are shown which perhaps represent a new unknown phase of  $\text{K}_3\text{Fe}(\text{SO}_4)_3$ , which has a melting endotherm (Fig. 6) at  $700^\circ\text{C}$ .

Subsequently, the potassium iron(III) trisulfate dissociates in the conventional way



and its dissociation continues beyond the closing temperature of the heating program ( $1050^\circ\text{C}$ ).

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