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A Phase Study of the Iron(III) Sulfate, Sodium Sulfate and Sodium Chloride System

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A phase diagram was drawn by using the results of a differential thermal analysis of the samples sealed in vicolglass and X-ray diffraction techniques undertaken in connection with the study of chlorine formation by the reaction of sodium chloride with sulfur dioxide and oxygen in the presence of iron compounds. In the two-component sodium sulfate - iron(III) sulfate system, the eutectic point was found at 562°C, the peritectic point, at 780°C, and the peritectoid point, at about 380°C. The former two values differ from those found by K. A. Bol' shakov et al. (*Zhur. Neorg. Khim.*, **8**, 2577 (1963)). In the trigonal diagram, two eutectic points were found, one at 465°C with a composition of about 13.5 mol.% iron sulfate, 53.5 mol.% sodium chloride and 33.0 mol.% sodium sulfate, and the other at 454°C with 15.0 mol.% iron(III) sulfate on the line of sodium chloride - iron(III) sulfate. It was confirmed that the peritectic point corresponding to the $Fe_2(SO_4)_3+Na_2SO_4(l)=2NaFe(SO_4)_2$ reaction shifted from 780°C on the line of sodium sulfate - iron(III) sulfate to 680°C on that of sodium chloride - iron(III) sulfate. From the diagram, the retarding tendency of the reaction rate of the final period of chlorine formation was attributed to diffusion control coming from the formation of solid phases.

The formation reaction of chlorine represented by the equation $2NaCl+SO_2+O_2=Na_2SO_4+Cl_2$ has previously been studied by the authors of this paper.[1] It was observed that the presence of iron compounds extremely accelerated the reaction rate and easily converted the system into the melt. This paper will give information about the phase change as the reaction proceeds. The phase diagram of the titled system is also expected to give fundamental data on the deposits produced at the medium temperature range in an oil furnace.

The titled system is a half of the four-component system iron(III) sulfate - sodium sulfate - sodium chloride - iron(III) chloride, which must be considered in the above-mentioned formation reaction of chlorine.

In order to draw the phase diagram, the differential thermal analysis (DTA) was performed in sealed cells, as it was inevitable in open apparatus for the composition of samples to change spontaneously, as a result of the decomposition, to form sulfur dioxide, sulfur trioxide and chlorine at temperatures above 600°C.

Apparatus and Experimental Methods

Reagents.—Chemically-pure sodium sulfate and sodium chloride were used after drying, while iron(III) sulfate was prepared from chemically-pure $Fe_2(SO_4)_3\cdot xH_2O\cdot yH_2SO_4$ by double drying processes; the first process involved drying at 180°C for two or three hours in an open vessel, and the second, drying at 450°C for an hour in a test tube, in which the dead space over the reagent was made as small as possible. The composition of the reagent prepared by these methods corresponded to $Fe_2(SO_4)_3\cdot 0.016Fe_2O_3$, and the X-ray diffraction pattern accorded with that in the literature.[2] The DTA cells were made of vicolglass; they were 40 mm. long, 4.7 mm. in inner diameter, and 0.7 mm. thick. Alumel-chromel thermocouples were used for the measurement of the differential temperature, and alumina powder was used as the standard substance. The temperature scale was calibrated at three points: the melting point of sodium chloride (801°C), the α, β transition point of potassium sulfate (583°C), and the transition point of silver chloride from $\alpha+\beta$ to γ (143°C). The ascending and descending speeds of the temperature were adjusted to 3°C per min. by the use of a photoelectric programmer. Generally, the first ascending curves were abandoned, and after holding at 900°C for an hour, the descending curves were recorded. From the temperatures under 150°C, the ascending curves were recorded again. Some samples which had the composition of iron(III) sulfate above 40 mol.% were heated up to 1000°C on account of their hard melting properties.

The compositions of samples were selected on the lines of 0, 3.3, 6.6, 10, 15, 20, 30, 40 and 50 mol.% iron(III) sulfate in the triangular diagram; these lines are close enough in composition that the nearest two compositions have difference of less than 10 mol.% for every component. Many samples were also taken up on the lines of sodium chloride - iron(III) sulfate and sodium sulfate - iron(III) sulfate.

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[1] K. Sugiyama and T. Takahashi, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **66**, 1773 (1963).

[2] J. V. Smith, A. S. Beward, L. G. Berry, B. Post, S. Weissmann and M. B. Lotz, "Index to the Powder Diffraction File," American Society for Testing and Materials, Philadelphia (1964), p. 605.

The analysis of DTA was carried out as usual; the temperature of the phase change was decided by the point of intersection of the build-up tangent and the corresponding ground line. After the DTA measurements, the samples were analyzed to give X-ray diffraction diagrams by Co K_α at room temperature.

Results and Discussion

The Sodium Sulfate and Iron(III) Sulfate System.—From the results shown in Fig. 1, the eutectic point B is found to be 562°C at 17.5 mol.% of iron(III) sulfate. The peritectic point, DF, at which the $Fe_2(SO_4)_3+Na_2SO_4(l)=2NaFe\cdot(SO_4)_2$ reaction occurs, is about 780°C, and the peritectoid point, KMN, is also found to be about 380°C (here the $NaFe(SO_4)_2+Na_2SO_4(l)=Na_3Fe(SO_4)_3$ reaction occurs).

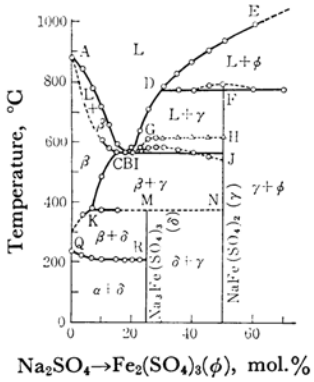

Fig. 1. The system Na_2SO_4-$Fe_2(SO_4)_3$.
GH and IJ lines refer to irreversible changes, and α, β refer to α and β sodium sulfate solid solutions respectively.

On the line of GH, the peaks of DTA curve were observable only in the run of ascending temperature, except for a few points near G. On the contrary, the peaks of the DTA curve on the line of IJ were observed only in the run of descending temperature, except for a few points near I.

According to Bol'shakov et al.,³⁾ who have reported on the same system, this system has the eutectic point at 620°C, the peritectic point at 680°C, the peritectoid point at 420°C, and the α, β transition point of a sodium sulfate solid solution at 220—228°C. Considerable discrepancies are found between Bol'shakov's results and those of the present paper. Though little description of the apparatus and experimental methods appeared in Bol'shakov's report, it is likely that the discrepancies arise from the dependence of the phase transition temperature on the pressure in the present experiment, or from the change in the composition of the sample on account of the decomposition in Bol'shakov's experiment.

In Fig. 2, the X-ray diffraction diagrams of the sodium sulfate - iron(III) sulfate system are drawn. The patterns of tri-sodium iron(III) tri-sulfate are found above 6.6 mol.% iron(III) sulfate; they increase in intensity up to 25 mol.%, above which the patterns of sodium iron(III) di-sulfate gradually increase to 50 mol.% iron-(III) sulfate.

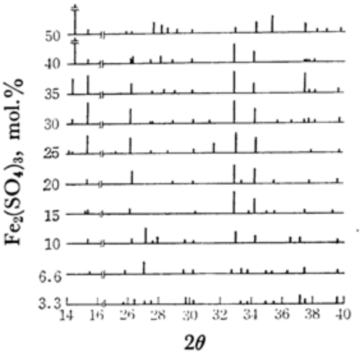

Fig. 2. X-ray diffraction diagrams of the system Na_2SO_4-$Fe_2(SO_4)_3$.

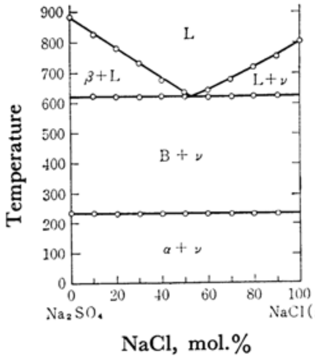

Fig. 3. The system Na_2SO_4-NaCl.

The Sodium Chloride and Sodium Sulfate System.—The phase diagram of this system, indicated in Fig. 3, is in good accordance with the results reported by Fedorov et al.⁴⁾

The Inner Territory of the Sodium Sulfate, Sodium Chloride and Iron(III) Sulfate System.—To represent variations in temperature as well as in composition, the sectional diagrams, which are cut along various mol.%'s of iron(III) sulfate, are indicated in Figs. 4 to 10. The phase boundary between the phase containing β-sodium sulfate, tri-sodium iron(III) tri-sulfate and sodium chloride and the phase containing tri-sodium iron(III) tri-sulfate, sodium iron(III) di-sulfate and sodium chloride was determined from the peaks of the

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3) K. A. Bol'shakov, P. I. Fedorov and N. I. Iliena, *Zhur. Neorg. Khim.*, **8**, 2577 (1963).

4) P. I. Fedorov and K. A. Bol'shakov, ibid., **4**, 893 (1959).

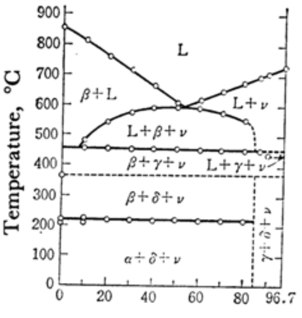

Fig. 4. Sectional diagram cut along the composition of 3.3 mol.% $Fe_2(SO_4)_3$.

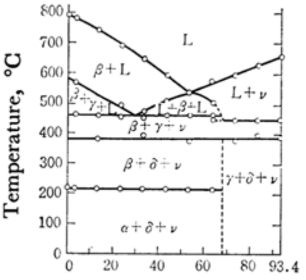

Fig. 5. Sectional diagram cut along the composition of 6.6 mol.% $Fe_2(SO_4)_3$.

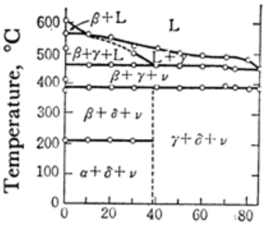

Fig. 6. Sectional diagram cut along the composition of 15 mol.% $Fe_2(SO_4)_3$.

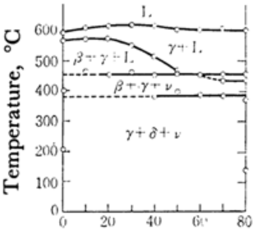

Fig. 7. Sectional diagram cut along the composition of 20 mol.% $Fe_2(SO_4)_3$.

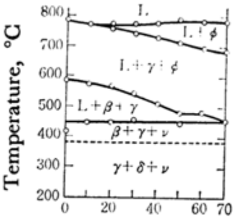

Fig. 8. Sectional diagram cut along the composition of 30 mol.% $Fe_2(SO_4)_3$.

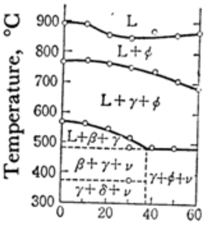

Fig. 9. Sectional diagram cut along the composition of 40 mol.% $Fe_2(SO_4)_3$.

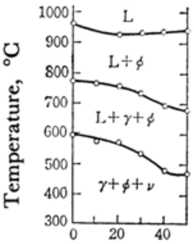

Fig. 10. Sectional diagram cut along the composition of 50 mol.% $Fe_2(SO_4)_3$.

α, β transition of sodium sulfate in DTA curves, as is shown in Figs. 4 to 6 by vertical dotted lines. The presence of iron(III) sulfate, tri-sodium iron(III) tri-sulfate and sodium iron(III) di-sulfate was detected by X-ray diffraction, in which the most distinct peaks by which to identify the respective compounds were found at 2θ values of 16.9°, 15.1° and 14.3° respectively.

From Figs. 7 to 10, it seems that the liquidus planes of the samples containing above 20 mol.% of iron(III) sulfate are influenced slightly by the variation in the mixing ratio of sodium sulfate and sodium chloride. The phase containing iron(III) sulfate is found over 30 mol.% of iron(III) sulfate at a high temperature and over 40 mol.% at room temperature, as is shown in Figs. 8 to 10. It may clearly be seen in Figs. 8 and 9 that the peritectic point, where the $Fe_2(SO_4)_3+Na_2SO_4=2NaFe(SO_4)_2$ reaction occurs, varies from the sodium sulfate and iron(III) sulfate side to the sodium chloride and iron(III) sulfate side, and that the maximum temperature difference of the both sides reaches about 100°C.

The first solid phase which separates on cooling

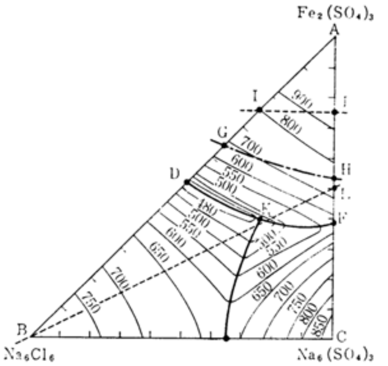

Fig. 11. Liquidus plane indicated by contour method.

is indicated by thick lines (DK, KF and KE) and a broken line (GH) in Fig. 11, in which the corners of the triangle are taken as 6 equivalent compounds—for example, Na_6Cl_6 instead of NaCl. The inner zone of AGH corresponds to the phase separating iron(III) sulfate first; GDKFH, to that separating sodium iron(III) di-sulfate; DBEK, to that separating sodium chloride, and EKFC, to that separating a β-sodium sulfate solid solution.

In Fig. 11, the dotted lines indicate the phase boundaries which are stable at room temperature; the inner zone of AJI corresponds to the phase containing sodium chloride, iron(III) sulfate and sodium iron(III) di-sulfate; IBHJ, to that containing sodium chloride, tri-sodium iron(III) tri-sulfate and sodium iron(III) di-sulfate; and LBC, to that containing sodium chloride, tri-sodium iron(III) tri-sulfate and α-sodium sulfate. The slender zone near the line of Na_6Cl_6 - $Fe_2(SO_4)_3$ is inferred to contain iron(III) chloride because of the stoichiometric discrepancy, but its presence could not be detected by DTA and X-ray diffraction.

In Fig. 11, the liquidus plane is also indicated by the method of the isothermal contour, and thick lines correspond to the ternary eutectic curves. It is found that the eutectic point, K, is 465°C, with a composition of about 13.5 mol.% iron(III) sulfate, 53.5 mol.% sodium chloride and 33 mol.% sodium sulfate. Another eutectic is also found at 454°C on the line of Na_6Cl_6-$Fe_2(SO_4)_3$, which has about 15 mol.% iron(III) sulfate. The characteristic low melting zone (450—490°C) distributes from the central region of the triangle to the Na_6Cl_6-$Fe_2(SO_4)_3$ line.

In the reaction of sodium chloride with sulfur dioxide, 20 to 40 wt.% pyrite was effectively added to sodium chloride in order to accelerate the reaction rate. When the composition containing 30 wt.% pyrite is considered, it corresponds to the liquidus point of about 660°C on the Na_6Cl_6-$Fe_2(SO_4)_3$ line in Fig. 11. In the course of the reaction, the composition will vary from the Na_6Cl_6-$Fe_2(SO_4)_3$ to the $Na_6(SO_4)_3$-$Fe_2(SO_4)_3$ line, parallel with the Na_6Cl_6-$Na_6(SO_4)_3$ line. If the temperature of the reaction is above 560°C, the whole system will be changed into the melt as the reaction proceeds. However, the system will have deposits of the β-sodium sulfate solid solution in the final step of the reaction if a temperature below 600°C is selected. These deposits of β-sodium sulfate are susceptible to interference with the diffusion of gas and liquid, as has been established by the previous data of the present authors.[1] On the other hand, the higher concentration of iron compounds will spread the attainable extent of the reaction, since the eutectic point of the $Na_6(SO_4)_3$-$Fe_2(SO_4)_3$ system is as low as 562°C. This is again supported by the previous results of the present authors.

As a whole, the state of the reaction system may be explained as being in close relation to the attainable extent and the velocity of the formation reaction of chlorine through the oxidation of sodium chloride and sulfur dioxide in the presence of iron compounds.

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