On the Double Salt of Sodium and Potassium Sulphates.

By

Kichiro Okada.

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Mixed sulphates of sodium and potassium occur as a mineral glaserite at Stassfurt in Germany. As to its composition and constitution there have been controversies; and a complete literature is to be found in an article by Retgers.[1] According to him, there is only one double salt of the sulphates of the formula, $K_3Na(SO_4)_2$, while Brandrowsky[2] has come to the conclusion that only one double salt of the composition, $2K_2SO_4.Na_2SO_4$, is formed from the solutions in which sodium and potassium salts are present in a molar proportion of 1 : 2 to 1 : 1; and has considered the double salt of Retgers to be nothing but a mixture of this double salt and patassium sulphate. The conclusion of Brandrowsky has been corroborated by Kubierschky,[3] and that of Retgers by Grossner.[4] van't Hoff and Barschall[5] have insisted in their view that glaserite is an extreme end of a long series of solid solutions, saturated with potassium sulphate, having the composition $K_3Na(SO_4)_2$.

Lastly Nacken[6] has corroboiated the existence of the double salt $K_3Na(SO_4)_2$, and found that the double salt dissolved sodium sulphate to a certain extent, the solubility increasing with temperature.

At the suggestion of Prof. Y. Osaka the writer has undertaken, from the stand-point of the phase rule, to determine the composition of the double salt, its relation to the solid solutions, and the temperature influence on the solid solutions, utilising the analytical method worked out in the preceeding article.

1 Zs. physik Chem., **6**, 205. (1890).

2 *Ibid.*, **17**, 240 (1895).

3 Berliner SitzBer, (1902), 404.

4 Zs. Kristallogr., **39**, 155 (1904).

5 Berliner SitzBer., (1903), 359; and Zs. physik. Chem., **56**, 212 (1906).

6 Berliner SitzBer., (1910), 1016.

Experiment.

About 10 grams of mixtures of sodium and potassium sulphates of various proportions were dissolved in 10 c.c. of water in a flask of a capacity of about 30 c.c., which was made to rotate in a thermostat for a period of 24 hours or more. The saturated solution was separated from the residue by an apparatus shown in Fig. 1. A is a so-called calsium chloride tube containing purified cotton, and B a receiver, communicating by a long side tube C with a pump. The apparatus was immersed in the thermostat to keep the solution at a constant temperature. After separating the mother liquor from the residue as much as possible by the action of the pump, the latter was pressed between filter paper and dried in an air bath. The solution was evaporated on a water bath to complete dryness. The samples thus obtained were analysed exactly as described in the preceeding article. The results were as follows:

Fig. 1.

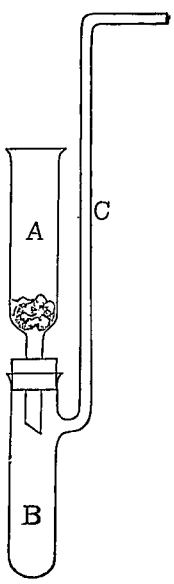


TABLE I.

Temperature: 15·0°.

No.	Sulphates in solution, in molar percentages.		Sulphates in residue, in molar percentages.	
	K_2SO_4	Na_2SO_4	K_2SO_4	Na_2SO_4
1	33·1	66·9	7·3	92·7
2	33·3	66·7	36·2	63·8
3	33·8	66·2	47·4	52·6
4	34·1	65·9	67·5	32·5
5	34·2	65·8	73·0	27·0
6	41·2	58·8	73·1	26·9
7	43·7	56·3	73·2	26·8
8	49·8	50·2	73·6	26·4
9	55·4	44·6	74·6	25·4
10	55·7	44·3	75·0	25·0
11	58·6	41·4	75·3	24·7
12	59·8	40·2	81·8	18·2
13	59·8	40·2	93·8	6·2

Table II.

Temperature: 25 0°

No.	Sulphates in solution, in molar percentages. K_2SO_4	Na_2SO_4	Sulphates in residue, in molar percentages. K_2SO_4	Na_2SO_4
1	19·8	80·2	5·8	94·2
2	20·1	79·9	19·3	80·8
3	19·7	80·3	21·2	78·8
4	20·2	79·3	55·9	44·1
5	20·6	79·4	70·0	30·0
6	24·1	75·9	71·9	28·1
7	28·9	71·1	71·7	28·3
8	31·8	68·2	71·6	28·4
9	32·2	67·8	72·0	28·0
10	34·8	65·2	72·0	28·0
11	36·1	63·9	72·2	27·8
12	42·0	58·0	72·2	27·8
13	46·2	53·8	72·2	27·8
14	58·7	41·3	74·2	25·8
15	60·8	39·2	80·5	19·5
16	59·6	40·4	85·6	14·4
17	60·9	39·1	91·7	8·3

Table III.

Temperature: 40 0.°

1	11·1	88·9	10·1	89·9
2	11·3	88·7	28·6	71·4
3	11·5	88·5	39·3	60·7
4	11·3	88·7	46·7	53·3
5	11·7	88·3	70·8	29·2
6	15·0	85·0	72·0	28·0
7	22·0	78·0	73·7	26·3
8	24·7	75·3	73·8	26·2
9	28·6	71·4	74·0	26·0
10	36·7	63·3	74·5	25·5
11	51·3	48·7	75·5	24·5
12	59·9	40·1	75·2	24·8
13	63·7	36·3	91·4	8·6

TABLE 4.

Temperature: 500°

No.	Sulphates in solution, in molar percentages. K_2SO_4	Na_2SO_4	Sulphates in residue, in molar percentages. K_2SO_4	Na_2SO_4
1	15·0	85·0	21·4	78·6
2	15·7	84·3	52·3	47·7
3	16·3	83·7	63·4	36·6
4	15·5	84·5	67·0	33·0
5	16·6	83·4	67·5	32·5
6	17·5	82·5	68·0	32·0
7	22·0	78·0	72·1	27·9
8	24·8	75·2	72·4	27·6
9	29·1	70·9	72·2	27·8
10	34·3	65·7	73·5	26·5

TABLE 5.

Temperature: 600°.

1	16·8	83·2	12·4	87·6
2	17·2	82·8	45·5	54·5
3	16·7	83·3	60·6	39·4
4	17·4	82·6	63·4	36·6
5	20·3	79·7	64·6	354
6	25·8	74·2	66·3	33·7
7	31·6	68·4	69·0	31·0
8	35·6	64·4	70·4	29·6
9	43·8	56·2	72·8	27·2
10	48·6	51·4	72·7	27·3
11	62·9	37·1	74·2	25·8
12	67·3	32·7	74·3	25·7
13	66·8	33·2	77·3	22·7
14	68·7	31·3	87·8	12·2

TABLE 6.

Temperature: 700°.

1	17·8	82·2	19·6	80·4
2	17·8	82·2	38·6	61·4

No.	Sulphates in solution, in molar percentages. K_2SO_4	Na_2SO_4	Sulphates in residue, in molar percentages. K_2SO_4	Na_2SO_4
3	17·4	82·6	47·3	52·7
4	18·0	82·0	56·2	43·8
5	17·8	82·2	68·4	31·6
6	17·3	82·7	68·9	31·1
7	18·3	81·7	69·3	30·7
8	19·1	80·9	69·3	30·7
9	23·3	77·7	70·8	29·2
10	28·6	71·4	72·3	27·7
11	34·5	65·5	73·1	26·9
12	34·7	65·3	73·2	26·8
13	55·3	44·7	75·2	24·8
14	68·9	31·1	75·8	24·2
15	69·4	30·6	82·6	17·4

TABLE 7.

Temperature: 80·0°.

1	19·2	80·8	16·3	83·7
2	19·7	80·3	46·8	53·2
3	19·2	80·8	51·0	49·0
4	19·8	80·2	59·5	40·5
5	20·1	79·9	68·5	31·5
6	20·0	80·0	70·1	29·9
7	24·2	75·8	72·0	28·0
8	25·3	74·7	71·6	28·4
9	30·6	69·4	74·1	25·9
10	38·3	61·7	74·9	25·1
11	51·2	48·8	75·2	24·8
12	64·2	35·8	74·9	25·1
13	70·4	29·4	87·4	12·6
14	70·7	29·3	93·0	7·0

These results are represented in square diagrams in Fig. 2 to 8. the horizontal side representing the composition of residue, and the vertical that of the salts in solution.

Fig. 2.

Temperature: 15·0°.

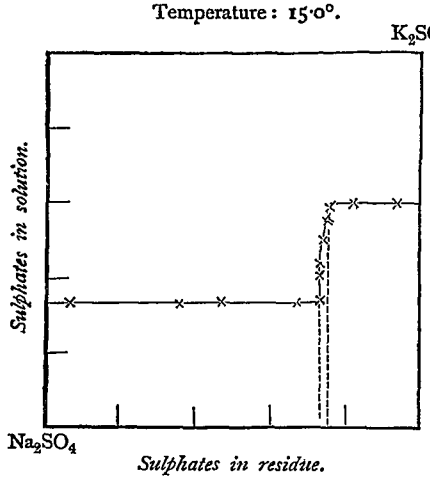


Fig. 3.

Temperature: 25·0°.

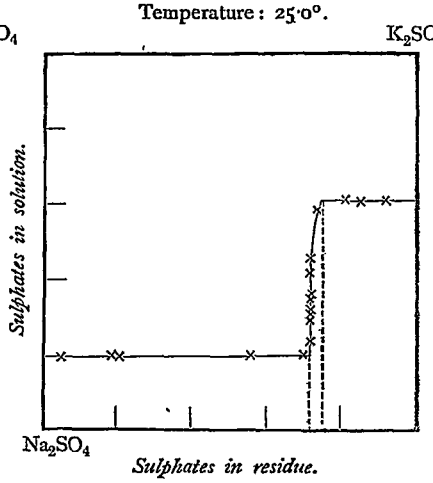


Fig. 4.

Temperature: 40.0°.

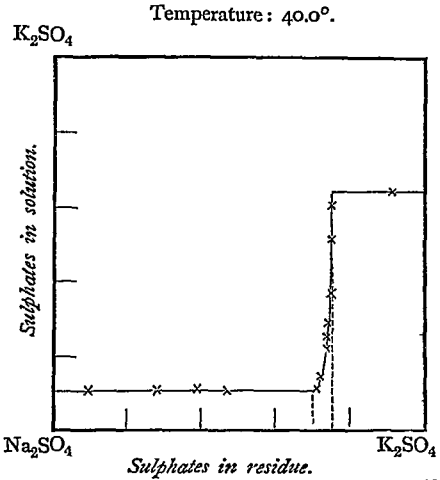


Fig. 5.

Temperature: 50 0°.

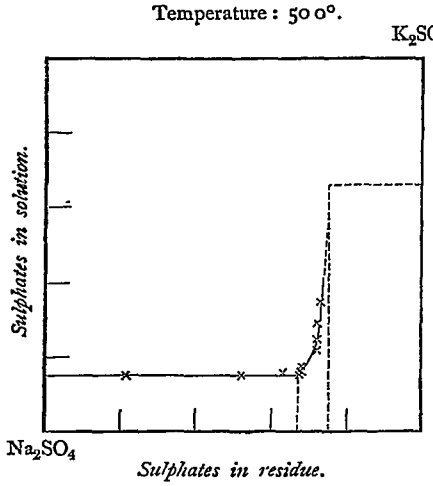


Fig. 6.

Temperature: 60·0°.

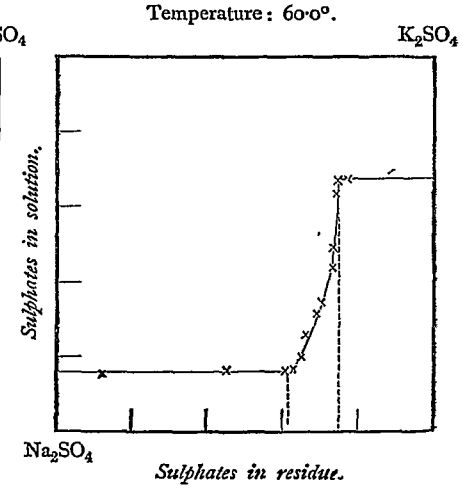


Fig. 7.

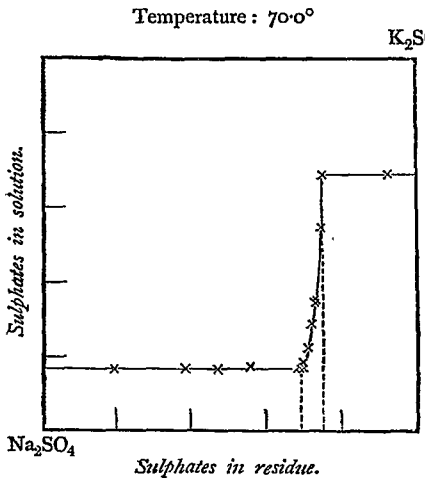
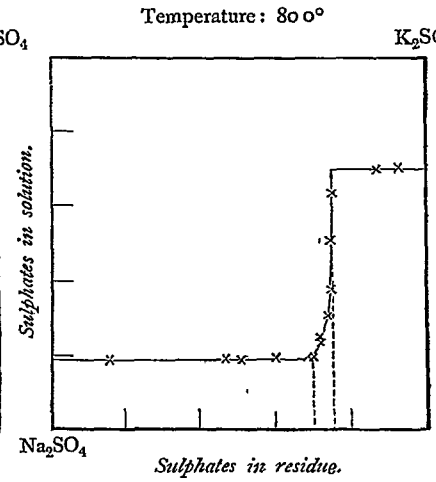


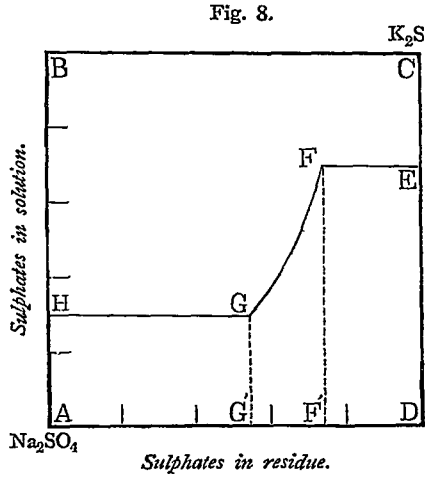
Fig. 8.



Discussion.

The curves in these seven figures have a general form as shown in Fig. 9,[1] where

Fig. 8.



C represents a pure saturated solution of potassium sulphate;

CE solution saturated with potassium sulphate together with a gradually increasing quantity of soduim sulphate;

EF solutions saturated with potossium sulphate and a residue represented by the point *F'*;

FG a solution, as the residue, having a series of solid solutions of which the composition varies from *F'* to *G'*;

GH solutions saturated with sodium sulphate and a residue represented by the point *G'*;

HA solutions saturated with sodium sulphate, with a gradually decreasing quantity of potassium sulphate;

A a pure saturated solution of sodium sulphate.

Now it is clear from the figure that at least one of the point *F'*

[1] The curve FG is concave to the residue axis at lower temperatures.

and G' must represent a double salt. The following table derived from Fig. 2 to 8 will decide.

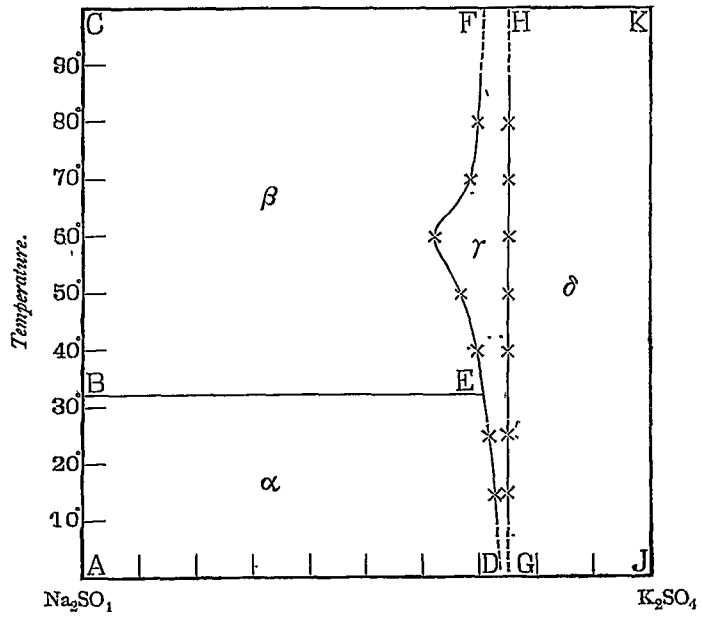
TABLE 8.

Temperature.	Composition of F', in molar percentages. K_2SO_4	Na_2SO_4	Composition of G', in molar percentages. K_2SO_4	Na_2SO_4	Difference.
15·0°	75·0	25·0	73·0	27·0	2·0
25·0°	75·0	25·0	71·7	28·3	3·3
40·0°	75·0	25·0	69·5	30·5	5·5
50·0°	(75·0)	(25·0)	66·7	33·3	(8·3)
60·0°	75·0	25·0	61·8	38·2	13·2
70·0°	75·0	25·0	68·8	31·2	6·2
80·0°	75·0	25·0	69·5	30·5	5·5

As seen from the table, the composition of G' varies with a change of temperature but that of F' does not; and it may be inferred that the residue represented by F' is a compound but the other not. The point F' just corresponds to the formula $K_3Na(SO_4)_2$, and the point G' represents the double salt saturated with sodium sulphate, and the curve GF has the double salt unsaturated with sodium sulphate as the residue.

To test the influence of temperature on the solubility of sodium sulphate in the double salt, the data in the fore-going table are graphically represented in Fig. 10. In the figure, B being the transition

Fig. 10.



temperature of sodium sulphate from decahydrate to anhydrous, namely 32·383°, *AB* represents the decahydrated sodium sulphate and *BC* the anhydrous. The curve *DEF* represents the double salt saturated with sodium sulphate, *GH* glaserite, and *JK* potasium sulphate. In the field α there exist decahydrated sodium sulphate and the double salt saturated with sodium sulphate, in β that solid solution and anhydrous sodium sulphate, in γ unsaturated solid solutions and in δ the double salt and potassium sulphate.

The results as a whole are concordant with those of Nacken as far as 60°; but above that temperature the field of the solid solution becomes narrower again, whereas Nacken assumed it to widen with the rise of temperature up to 180°.

Summary.

1. Sodium and potassium sulphates form a double salt of the formula $K_3Na(SO_4)_2$.

2. This double salt dissolves sodium sulphate as a solid solution but not potassium sulphate.

3. The limit of the solid solutions has been determined for the temperature interval from 15° to 80°.

In conclution I wish to express my sincere thanks to Prof. Y. Osaka for his valuable suggestions and kind instruction.