

XXX.—*Heterogeneous Equilibria between the Sulphates and Nitrates of Sodium and Potassium and their Aqueous Solutions. Part I. The Ternary Systems.*

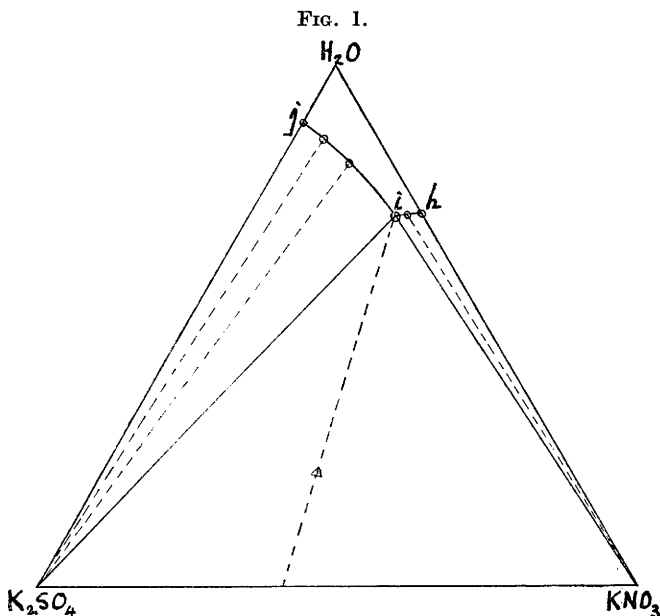
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DURING the course of an investigation of the quaternary system  $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{NaNO}_3-\text{K}_2\text{SO}_4-\text{KNO}_3$  at  $25^\circ$  and  $90^\circ$ , it became necessary to investigate and revise some of the ternary systems involved. The subject of the present paper is to record the data so obtained and to sum up briefly all other information available about the isothermal relations in the four ternary systems which form the basis of the above quaternary system. In the isotherms at  $90^\circ$ , only the invariant points have been determined. The solubilities of single salts have been selected from Seidell's "Solubilities of Inorganic and Organic Substances." The vapour phase is always assumed to be absent and the whole subject is treated from the point of view of condensed systems at atmospheric pressure.

EXPERIMENTAL.

All the salts used were carefully purified by repeated crystallisation and their purity was checked by a number of analyses before use. For the determination of solubility, various complexes were vigorously stirred up to equilibrium in wide tubes immersed in water- and oil-thermostats kept constant within  $0.02^\circ$  at  $25^\circ$  and within  $0.2^\circ$  at  $90^\circ$ . The usual time given was about 40 hours at  $25^\circ$  and about 10 hours at  $90^\circ$ . The compositions of the solutions when equilibrium was established were determined by withdrawing

portions of them by means of pipettes heated previously to the temperatures of the baths, filtering, and weighing in stoppered bottles and analysing the solutions. The moist residue was weighed separately and analysed. The potassium ion was determined by the cobaltinitrite method, sulphate weighed as barium sulphate, and nitrate estimated by a modified method of Schlösing. All these methods were checked beforehand by a large number of estimations in mixtures of sodium sulphate, sodium nitrate, potassium sulphate, and potassium nitrate of known compositions. The amounts of sodium and water were determined by difference. In



some cases all the salts were converted into the chlorides and the analytical results checked in this way.

The thermometers were all compared with those standardised at the National Physical Laboratory, Teddington.

*The System Water-Potassium Sulphate-Potassium Nitrate.*—This belongs to the simplest type of ternary system, neither double salts nor salt hydrates occurring in it. The system at 25° is represented graphically in Fig. 1, and the experimental data for the two temperatures are in Table I.

*The system water-sodium nitrate-potassium nitrate* has been worked out by Reinders (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 1065) at 25°. The compositions of the binary and ternary invariant solutions at 90° are in Table II.

TABLE I.  
Composition by weight percentage.

Temp.	Solution.		Rest.		Solid phases.
	% K <sub>2</sub> SO <sub>4</sub> .	% KNO <sub>3</sub> .	% K <sub>2</sub> SO <sub>4</sub> .	% KNO <sub>3</sub> .	
25°	10.74	0	—	—	K <sub>2</sub> SO <sub>4</sub>
"	8.85	4.82	—	—	"
"	6.89	11.05	—	—	"
"	4.45	23.99	43.18	36.75	K <sub>2</sub> SO <sub>4</sub> + KNO <sub>3</sub>
"	1.98	26.01	—	—	KNO <sub>3</sub>
"	0	27.97	—	—	"
90°	18.57	0	—	—	K <sub>2</sub> SO <sub>4</sub>
"	0.63	65.92	—	—	K <sub>2</sub> SO <sub>4</sub> + KNO <sub>3</sub>
"	0	66.90	—	—	KNO <sub>3</sub>

TABLE II.  
Composition by weight percentage.

% NaNO <sub>3</sub> .	% KNO <sub>3</sub> .	Solid phases.
61.65	0	NaNO <sub>3</sub>
37.57	45.26	NaNO <sub>3</sub> + KNO <sub>3</sub>
0	66.90	KNO <sub>3</sub>

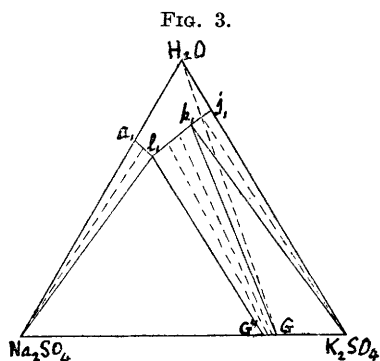
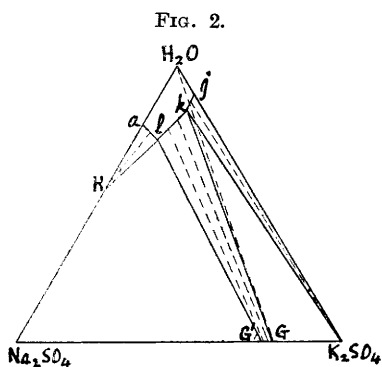
The system water-potassium sulphate-sodium sulphate is complicated by the existence of a double sulphate of sodium and potassium known as the mineral glaserite. As to the composition of this compound, there have been controversies from time to time. Its correct composition was first reported by Penny (*Phil. Mag.*, 1855, **10**, 401), who assigned the formula  $3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$  to it and after whom it is sometimes called Penny's double salt. Penny's results were corroborated by some authors, whilst several double sulphates of sodium and potassium of different compositions were subsequently described by various investigators. A complete literature on this subject can be found in a paper by Retgers (*Z. physikal. Chem.*, 1890, **6**, 205). van 't Hoff and Barschall (*Berlin. Sitzungsber.*, 1903, 359; *Z. physikal. Chem.*, 1906, **56**, 212) put forward the view that glaserite is an extreme limit of a series of solid solutions saturated with potassium sulphate having the composition  $\text{K}_3\text{Na}(\text{SO}_4)_2$ . Nacken (*Berlin. Sitzungsber.*, 1910, 1016) has confirmed the existence of the double salt  $\text{K}_3\text{Na}(\text{SO}_4)_2$  and has found that it dissolves sodium sulphate as a solid solution up to a certain extent. His results have been confirmed recently by Okada (*Mem. Coll. Sci.*, 1914, **1**, 95). Whereas Nacken assumes that the solubility of sodium sulphate in glaserite increases with temperature, Okada has shown that it increases to a temperature of 60°, where it reaches a maximum, and above that temperature the field of solid solutions becomes narrower again. The system  $\text{H}_2\text{O}-\text{K}_2\text{SO}_4-\text{Na}_2\text{SO}_4$  at 25° and 90° is shown in Figs. 2 and 3

respectively. The data for this system at these two temperatures are in Table III.

TABLE III.  
Composition by weight percentage.

Temp.	% Na <sub>2</sub> SO <sub>4</sub> .	% K <sub>2</sub> SO <sub>4</sub> .	Solid phases.
25°	21.84	0	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O
"	19.93*	7.06	{ Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O + mixed crystals of K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> and Na <sub>2</sub> SO <sub>4</sub>
"	5.58*	11.27	{ K <sub>2</sub> SO <sub>4</sub> + K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub>
"	0	10.74	K <sub>2</sub> SO <sub>4</sub>
90°	29.90	0	Na <sub>2</sub> SO <sub>4</sub>
"	27.05	8.33	{ Na <sub>2</sub> SO <sub>4</sub> + mixed crystals of Na <sub>2</sub> SO <sub>4</sub> and K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub>
"	9.23	14.97	{ K <sub>2</sub> SO <sub>4</sub> + K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub>
"	0	18.57	K <sub>2</sub> SO <sub>4</sub>

\* Meyerhoffer and Saunders, *Z. physikal. Chem.*, 1899, **28**, 482.



The points H and G (Figs. 2 and 3) represent the compositions of pure Glauber's salt and pure glaserite, respectively. The point G' (Fig. 2) represents the composition of the solid solution containing the maximum amount of sodium sulphate which glaserite can dissolve at 25°. Similarly the point G'' (Fig. 3) represents the composition of the solid solution which is formed by dissolving the maximum amount of sodium sulphate in glaserite at 90°. The compositions of G, G', and G'' are given in Table IV, both in terms of weight (*w*) and molar (*m*) percentages.

TABLE IV.

Temp. 25° :	Comp. of G.		Comp. of G'.		Diff.
	K <sub>2</sub> SO <sub>4</sub> .	Na <sub>2</sub> SO <sub>4</sub> .	K <sub>2</sub> SO <sub>4</sub> .	Na <sub>2</sub> SO <sub>4</sub> .	
<i>m</i> .....	75.0	25.0	71.7	28.3	3.3
<i>w</i> .....	78.6	21.4	75.7	24.3	2.9
Temp. 90° :	Comp. of G.		Comp. of G''.		Diff.
	K <sub>2</sub> SO <sub>4</sub> .	Na <sub>2</sub> SO <sub>4</sub> .	K <sub>2</sub> SO <sub>4</sub> .	Na <sub>2</sub> SO <sub>4</sub> .	
<i>m</i> .....	75.0	25.0	70.5	29.5	4.5
<i>w</i> .....	78.6	21.4	74.6	25.4	4.0



salts, sodium sulphate and sodium nitrate. The system at 25° is shown in Fig. 4, and the data for this system at the two temperatures are in Table V.

TABLE V.  
Composition by weight percentage.

Temp.	Solution.		Rest.		Solid phases.
	% Na <sub>2</sub> SO <sub>4</sub> .	% NaNO <sub>3</sub> .	% Na <sub>2</sub> SO <sub>4</sub> .	% NaNO <sub>3</sub> .	
25°	21.84	0	—	—	Na <sub>2</sub> SO <sub>4</sub> .10H <sub>2</sub> O
"	17.52	7.48	23.37	6.15	Na <sub>2</sub> SO <sub>4</sub> ,"
"	15.70	23.43	24.82	16.58	Na <sub>2</sub> SO <sub>4</sub> .10H <sub>2</sub> O + Na <sub>2</sub> SO
"	15.43	24.06	34.43	18.40	Na <sub>2</sub> SO <sub>4</sub>
"	14.15	25.96	39.87	20.45	Na <sub>2</sub> SO <sub>4</sub> + D <sub>1</sub>
"	11.88	28.46	30.00	31.05	D <sub>1</sub>
"	9.04	32.68	27.44	33.46	"
"	5.42	39.71	29.39	37.52	"
"	3.01	45.87	24.63	62.90	D <sub>1</sub> + NaNO <sub>3</sub>
"	0	47.69	—	—	NaNO <sub>3</sub>
90°	29.90	0	—	—	Na <sub>2</sub> SO <sub>4</sub>
"	2.53	58.66	—	—	Na <sub>2</sub> SO <sub>4</sub> + NaNO <sub>3</sub>
"	61.65	0	—	—	NaNO <sub>3</sub>

Composition of D<sub>1</sub> = Na<sub>2</sub>SO<sub>4</sub>, 57.96%; NaNO<sub>3</sub>, 34.68%; H<sub>2</sub>O, 7.36%.

The points H and D<sub>1</sub> (Fig. 4) represent the compositions of pure Glauber's salt and pure darapskite, respectively. The point D<sub>2</sub> (Fig. 4) represents the composition of the supposed anhydrous double salt of Massink and the point *d* his supposed ternary isothermal invariant point at which, according to him, the solution is in equilibrium with darapskite and the anhydrous double salt D<sub>2</sub>. Not only has this solution been found to be saturated with darapskite alone, but on isothermal evaporation of unsaturated solutions at 25° which theoretically ought to have deposited the anhydrous double salt D<sub>2</sub>, if it could exist, darapskite has been found to be precipitated as the first solid. Thus an unsaturated solution of the composition *i* (Fig. 4) on evaporation at 25°, according to Massink, should deposit the anhydrous double salt D<sub>2</sub> as the first solid and should continue to do so until the point *d* is reached. This it does not do. Instead, however, it deposits darapskite, which comes down in very fine, needle-shaped crystals, readily distinguishable with the naked eye. Besides the double salt D<sub>2</sub>, Massink (*loc. cit.*) describes another anhydrous double salt of the formula 3NaNO<sub>3</sub>.2Na<sub>2</sub>SO<sub>4</sub> at 35°. It may be noted that he has determined the compositions of these two anhydrous double salts from one or two analyses of the solution and the wet residue in each case, which in themselves are not sufficient. The improbability of the existence of these two anhydrous double salts in this system is further manifest from the following considerations. It has been

alleged by Massink himself that these two anhydrous double salts do not exist at lower temperatures. According to him, the transition temperatures which mark the lower stability limits to the existence of the two anhydrous double salts lie somewhere between  $20^{\circ}$  and  $35^{\circ}$ . Further, it has been shown by Schreinemakers (*Z. physikal. Chem.*, 1909, **65**, 553) that if two anhydrous salts can form an anhydrous double salt at a certain temperature in the binary system, formed by these two salts, they will do so at the same temperature in all ternary systems formed by the addition of any liquid component to the above binary system, and the solubility curves of the two salts will be interrupted by that of the double salt in all these systems at this temperature. The converse of this principle has been very recently applied by Freeth (*J. Physical Chem.*, 1925, **29**, 1497) in the deduction of the type of a two-component system by the addition of a third component, from which it follows that if above a certain temperature in the ternary system  $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{NaNO}_3$  the solubility curves of sodium sulphate and sodium nitrate are interrupted by that of an anhydrous double salt, this will be the case also in the binary system  $\text{Na}_2\text{SO}_4-\text{NaNO}_3$ . Since the solution does not participate in the formation of the anhydrous double salt, the transition temperature of this binary compound is independent of the number of components of the system, *i.e.*, it is the same in all systems whether binary, ternary, or quaternary. It is clear, therefore, that at temperatures above  $35^{\circ}$  the two anhydrous double salts of Massink, if they can exist at all, must be formed in the ternary system  $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{NaNO}_3$  as also in the binary system  $\text{Na}_2\text{SO}_4-\text{NaNO}_3$ . From an investigation of the quaternary system  $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{NaNO}_3-\text{K}_2\text{SO}_4-\text{KNO}_3$  at  $90^{\circ}$  the author has been led to the conclusion that no such double salts exist in the ternary system  $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{NaNO}_3$  at this temperature, the only solid phases being the two anhydrous salts, sodium sulphate and sodium nitrate. This is in complete accord with the very recent investigations of Perman and Harrison (*J.*, 1924, **125**, 365) of the binary system  $\text{Na}_2\text{SO}_4-\text{NaNO}_3$ .

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