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THE SYSTEM Na_2SO_4–NaF–NaCl–H_2O. II. THE QUATERNARY SYSTEM AT 25 AND 35°[1]

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The quaternary system Na_2SO_4–NaF–NaCl–H_2O is derived from three ternary systems, each composed of two of the above salts and water. The data on these three systems were presented in the first part of this paper.[2] At a given temperature, proceeding from each univariant point in these systems, where two solid phases coexist, there is a solubility curve ending at a point where a third solid phase appears. We have determined the solubility relations and the solid phases for the quaternary system at the temperatures 25 and 35°.

The chief experimental difficulty in the investigation was to obtain the gross composition of the residues, because it is impossible to free them entirely from solution. At 35°, since all the solids are anhydrous, it was possible to filter the solids rapidly on a warmed Gooch crucible, after removing a sample of the solution for analysis. The solids were washed quickly with alcohol and dried between filter papers. At 25°, except where noted, we analyzed wet residues. Since the composition of the solution is known, the gross composition of the solid residues may be calculated.[3] By making a sufficient number of such determinations, it is possible to decide whether one is at a univariant point (with three solid phases and constant solubility) or on a divariant curve (with two solid phases and varying solubility). We made use of the optical properties of the crystals to determine qualitatively the number and kind of solid phases as a check on the analytical data.

The results are given in Table I. The composition of the residue free from mother liquor is given in all cases, whether determined directly by analysis or calculated after analysis of solution and wet residue. Sodium fluoride is only slightly soluble in the more concentrated solutions of sodium sulfate and chloride. Whenever less than 0.1% was found, it is reported as a trace.

To show the results in a diagram, we have plotted the solubilities of the three salts along three axes which make an angle of 120° with each other. In ternary systems it is convenient to represent isotherms in an equilateral triangle in which composition of both solutions and residues may be plotted.

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[1] The data presented in this paper constitute a portion of a Dissertation presented to the Graduate School of Yale University by J. F. Schairer, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1928.

[2] Foote and Schairer, THIS JOURNAL, 52, 4202 (1930).

[3] This method can be used only when the solid phases do not contain all four components.

TABLE I

SOLUBILITY ISOTHERMS—SYSTEM Na_2SO_4–NaF–NaCl–H_2O

	Solution			Residue			
No.	% Na_2SO_4	% NaF	% NaCl	% Na_2SO_4	% NaF	% NaCl	Solid phases
				$T = 35°$			
1	6.14	Tr.	23.37	65.39	0.96	33.65	Na_2SO_4 + NaCl + Ds[a]
2	5.95	Tr.	23.54	71.03	6.68	22.29	Na_2SO_4 + NaCl + Ds
3	0.49	0.12	26.08	45.88	15.21	38.91	NaF + NaCl + Ds
4	.41	.30	26.03	10.68	16.88	72.44	NaF + NaCl + Ds
5	.17	.31	26.18	14.77	74.31	10.92	NaF + NaCl + Ds
6	.24	.43	22.36	45 11	53.89	1.00	NaF + Ds
7	.80	.49	21.05	70.33	27.37	2.30	NaF + Ds
8	1.43	.80	16.14	56.52	43.21	0.27	NaF + Ds
9	2.67	1.27	10.71	61.77	38.23	None	NaF + Ds
10	4.84	1.80	5.42	68.42	31.58	None	NaF + Ds
11	6.89	Tr.	22.31	86.27	10.02	3.71	Na_2SO_4 + Ds
12	8.73	0.35	19.47	87.46	7.66	4.88	Na_2SO_4 + Ds
13	14.13	0.62	13.60	85.15	13.37	1.48	Na_2SO_4 + Ds
14	21.39	Tr.	8.09	85.70	13.46	0.84	Na_2SO_4 + Ds
15	3.66	0.46	24.32	57.55	13.71	28.69	NaCl + Ds
16	3.22	.14	24.81	53.48	13.50	33.02	NaCl + Ds
17	20.83	.23	4.93	79.39	20.59	None	Ds
18	17.66	.13	8.55	79.48	20.52	None	Ds
19	7.46	.75	7.26	77.78	22.22	None	Ds
20	5.08	.24	14.59	77.68	22.32	None	Ds
21	4.35	0.19	18.57	77.02	22.67	0.31	Ds
22	8.17	Tr.	18.38	76.70	20.76	2.53	Ds
23	2.97	0.20	23.36	75.37	21.02	3.61	Ds
24	4.39	0.61	21.64	75.51	18.48	6.01	Ds
25	1.51	Tr.	23.34	74.68	19.03	6.29	Ds
				$T = 25°$			
1	0.21	0.43	25.96	11.98	11.30	76.72	NaF + NaCl + Ds[a]
2	0.50	0.23	25.93	56.51	21.48	22.01	NaF + NaCl + Ds
3	0.43	0.27	25.90	11.27	74.00	14.73	NaF + NaCl + Ds
4	7.04	Tr.	22.71	66.56	12.25	21.19	Na_2SO_4 + NaCl + Ds
5	6.82	0.10	22.77	19.43	2.98	77.59	Na_2SO_4 + NaCl + Ds
6	6.98	Tr.	22.73	86.75	2.87	10.38	Na_2SO_4 + NaCl + Ds
7	14.75	Tr.	13.79	66.25[b]	3.98	None	Na_2SO_4 + $Na_2SO_4 \cdot 10H_2O$ + Ds
8	14.76	Tr.	13.78	76.92[b]	20.41	None	Na_2SO_4 + $Na_2SO_4 \cdot 10H_2O$ + Ds
9	5.23	Tr.	23.61	43.84	10.95	45.21	NaCl + Ds
10	9.72	Tr.	19.29	90.41	7.57	2.02	Na_2SO_4 + Ds
11	4.35	0.60	21.48	77.64	21.67	0.69	Ds
12	4.47	Tr.	18.41	77.31	22.69	None	Ds
13	4.60	0.77	14.35	76.85	23.15	None	Ds
14	7.71	0.69	6.98	77.17	22.83	None	Ds

[a] Ds = double salt $Na_2SO_4 \cdot NaF$. (This is capable of taking up a limited amount of NaCl in solid solution which replaces an equivalent quantity of NaF. The pure double salt contains 77.18% Na_2SO_4.)

[b] This residue was air dried for analysis. The others were analyzed wet and the composition of the dried residues, as given in the table, was calculated.

However, in a quaternary system, it is not feasible to represent the composition of both solutions and residues by a single diagram. We have therefore represented the composition of residues by means of a separate triangular diagram used in conjunction with the solubility diagram to show the relations of residues to their solutions. This is entirely satisfactory when the residues are anhydrous, which is the case at 35°. At 25° this method of representing residues cannot be used, as both anhydrous Na_2SO_4 and $Na_2SO_4 \cdot 10H_2O$ are present.

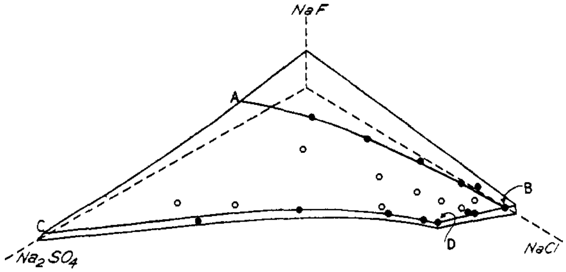

Fig. 1.—System Na_2SO_4–NaF–NaCl–H_2O. Solubility isotherm at 35°.

The solubility data are plotted in Figs. 1 (35° isotherm) and 2 (25° isotherm). At univariant points, the average result of the several determinations is represented. Some univariant points taken from the ternary systems have been displaced outward slightly to make the diagram clear, since they almost coincide with the corresponding quaternary points.

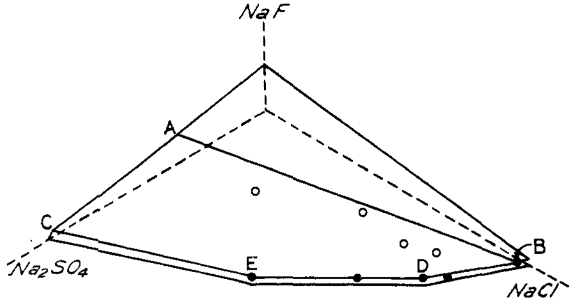

Fig. 2.—System Na_2SO_4–NaF–NaCl–H_2O. Solubility isotherm at 25°.

At 35° (Fig. 1) the double salt (in which some NaCl replaces NaF) is stable throughout the area ABDC. The solubility results obtained in this area (Nos. 17–25 in Table I) are plotted as circles. At the univariant points B and D, three solid phases coexist in equilibrium with solution. Univariant points and points on the three curves are plotted as black dots. At 25° (Fig. 2), the relations are similar but an additional univariant point E exists, where the solid phases are double salt, Na_2SO_4 and $Na_2SO_4 \cdot 10H_2O$.

At this point the double salt contains no appreciable amount of NaCl. Only a few determinations were made at 25°, since the general relations were already clear.

The residues at 35°, so far as they contain all three salts, are plotted in Fig. 3. In considering this diagram, it must be remembered that the double salt can take up a limited amount of chloride in solid solution, which replaces an equivalent amount of fluoride. This replacement only becomes appreciable in the presence of considerable amounts of sodium chloride in solution. (Nos. 22–25 of Table I.) The composition of the double salt is therefore variable and represented by the line ABC. The maximum amount of solid solution, represented by C, is not accurately known, but is undoubtedly a function of temperature. The solution yielding the maximum is very probably at the univariant point where the solid phases are Na_2SO_4, NaCl and double salt. In the table of data at 35° (Table I), Nos. 17–21 contain little or no chloride in the double salt and their composition falls very close to the point A of Fig. 3. The other residues consisting of double salt showing appreciable solid solution (Nos. 22–25, Table I) are plotted. Two of them are somewhat off the line AC, showing that these were slightly contaminated with sodium chloride from the solution, though their solubility shows quite definitely that but a single phase was present. The areas ACD, ABE and BCF (Fig. 3) correspond to mixtures of Na_2SO_4 with double salt, NaF with double salt and NaCl with double salt, respectively. The numbered points refer to the numbers in Table I at 35°.

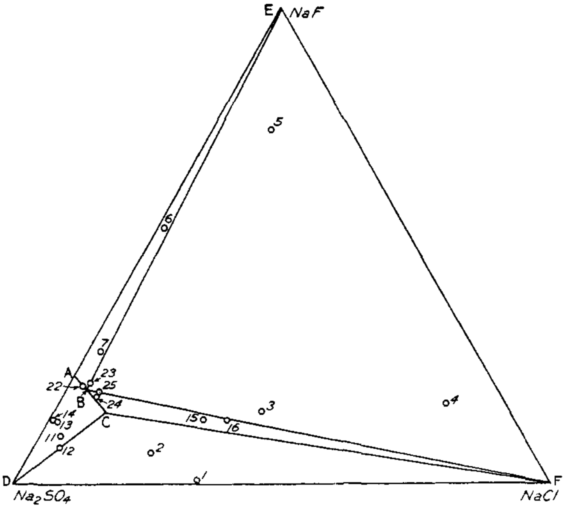

Fig. 3.—Composition of solid phases in equilibrium with solutions at 35°.

The residues in equilibrium with solutions at 25° show the same general relations. Complete representation of the residues on an equilateral triangle is not possible because anhydrous Na_2SO_4 and $Na_2SO_4 \cdot 10H_2O$ are present in some mixtures.

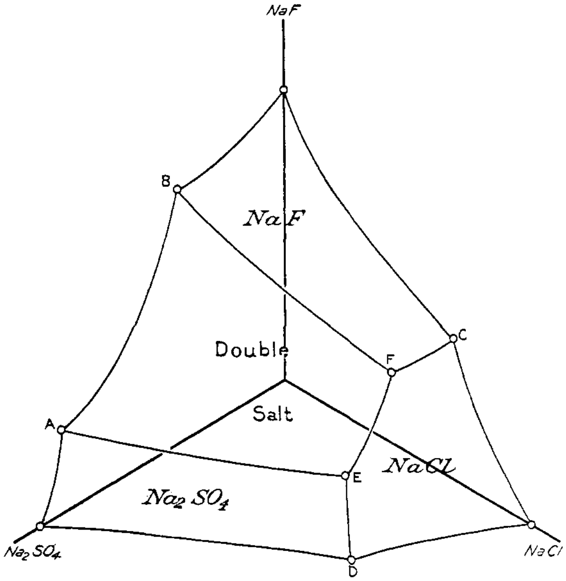

Fig. 4.—Hypothetical quaternary isotherm assuming that no triple salt appears.

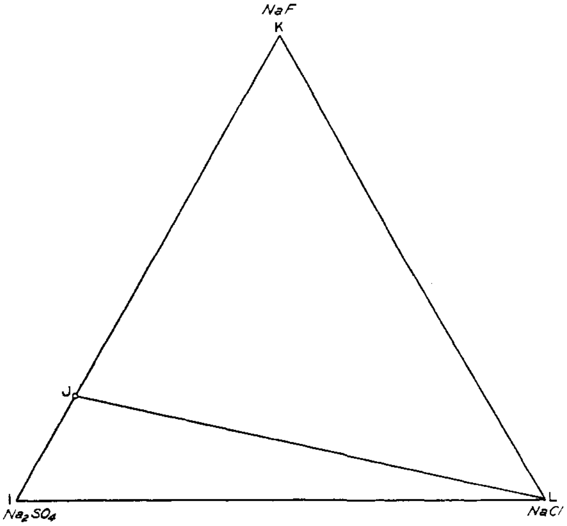

Fig. 5.—Composition of solid phases in equilibrium with solutions of Fig. 4.

There was a strong probability at the outset of the work that the mineral sulfohalite ($2Na_2SO_4 \cdot NaCl \cdot NaF$) might appear as one of the solid phases at the temperatures investigated. If this had appeared, it should be one of the solid phases in a portion of the area ABDC (Fig. 1). Then at the point B and possibly at D it would be one of the three solid phases. There would also be two other univariant points each with three solid phases and the corresponding divariant curves. It can be shown by considering the relation between solutions and residues that the solid phase $2Na_2SO_4 \cdot NaCl \cdot NaF$ did not appear at the temperatures investigated and that the solid phase in the area ABDC (Figs. 1 and 2) of the two investigated isotherms is not pure double salt $Na_2SO_4 \cdot NaF$ but a solid solution in which a limited part of the fluoride is replaced by chloride.

Let us assume that no triple salt appears in the quaternary system and that only the double salt $Na_2SO_4 \cdot NaF$ (with no solid solution) and the three single salts appear. Then the hypothetical solubility relations at some constant temperature are represented diagrammatically in Fig. 4. The assumed values for solubilities used to prepare Fig. 4 were so chosen as to prevent crowding of lines and points for clarity in presentation. Then the residues in equilibrium with such solutions may be shown on an equilateral triangle, Fig. 5. J represents the composition $Na_2SO_4 \cdot NaF$. If the assumed solubility relations were correct, all residues whose composition lay in the area IJL (Fig. 5) should have the same solubility (represented by E of Fig. 4) and similarly all those in the area JKL (Fig. 5) should have the solubility represented by F (Fig. 4).

By examining the actual data given in Table I and presented graphically in Figs. 1, 2 and 3, we find that the experimental data do not fit the assumption we have made.

If we assume that a triple salt $2Na_2SO_4 \cdot NaCl \cdot NaF$ appears and that the other solid phases in the quaternary system are pure double salt $Na_2SO_4 \cdot NaF$ and the single salts, these hypothetical relations can be shown diagrammatically in Fig. 6 (assumed values chosen to prevent crowding in the figure). The composition of all residues may be shown in Fig. 7. J represents the composition $Na_2SO_4 \cdot NaF$ and M the composition $2Na_2SO_4 \cdot NaCl \cdot NaF$. If the assumed solubility relations were correct, all residues whose composition lay in the areas IJM, JMK, MKL and IML (Fig. 7), respectively, would have the solubilities H, G, F and E (Fig. 6), respectively.

Again, examining the actual data given in Table I and presented graphically in Figs. 1, 2 and 3, we find that the experimental data are not in accord with the assumption made.

The experimental data show that at the temperatures investigated no triple salt forms and that in the quaternary system the double salt $Na_2SO_4 \cdot NaF$ has a limited part of its fluoride replaced by chloride. This fact was confirmed by microscopic examination. The replacement of fluoride by chloride raises the indices of refraction of the double salt.

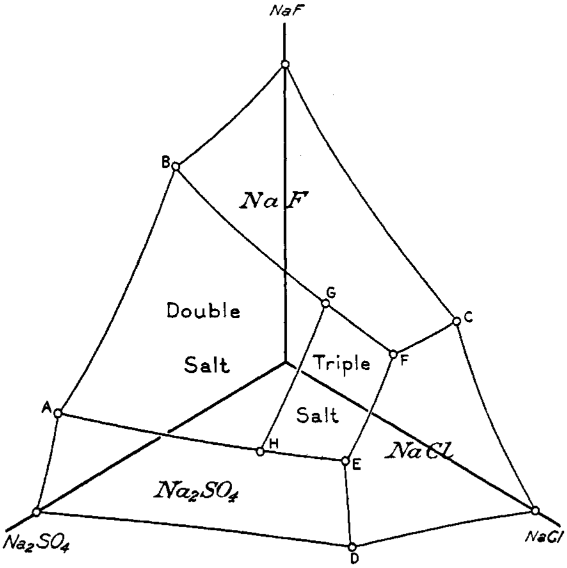

Fig. 6.—Hypothetical quaternary isotherm assuming existence of a triple salt $2Na_2SO_4 \cdot NaF \cdot NaCl$.

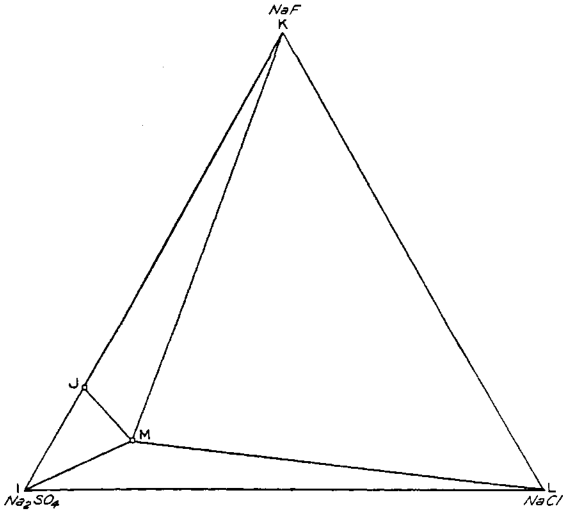

Fig. 7.—Composition of solid phases in equilibrium with solutions of Fig. 6.

In two cases after equilibrium had been reached at the points B and D (Figs. 1 and 2), we introduced a small amount of the natural mineral (sulfohalite $2Na_2SO_4{\cdot}NaF{\cdot}NaCl$ from Searles Lake, California) into the equilibrium bottles, which were again shaken at constant temperature. This was done to overcome any possible metastable condition and was without effect on the solubility or nature of solid phases present.

Sulfohalite.—We obtained several small crystals of the natural mineral, sulfohalite, from the U. S. National Museum (Museum No. 93,659). These crystals from Searles Lake, California, all proved quite unsuitable for chemical study owing to the very numerous and well distributed tiny laths and grains of an impurity. The sulfohalite crystals were sharp octahedrons, optically isotropic, $n_{\mathrm{Na}} = 1.454$. Sulfohalite is undoubtedly a distinct mineral. It is well crystallized and optically distinct from all other mineral species. Both Penfield[4] and Gale and Hicks[5] give its composition as $2Na_2SO_4{\cdot}NaF{\cdot}NaCl$. It might be supposed that the mineral represented an extreme case of solid solution in which the replacement of fluoride by chloride was by chance 1:1. The mineral, however, is isometric while the solid solution is hexagonal rhombohedral. It seems very unlikely that sulfohalite might appear at a transition temperature above 35°, since Teeple[6] has shown that the brine which permeates the entire salt deposit at Searles Lake is uniformly at 23° throughout the year. Our isotherms show no indication of the mineral between 25 and 35°. If it exists in stable equilibrium, it is likely that this can only be the case below 25°, which can be determined by further isotherms at lower temperatures.

Summary

Solubility isotherms for the quaternary system Na_2SO_4–NaF–NaCl–H_2O have been determined at 25 and 35°. At these temperatures, the double salt $Na_2SO_4{\cdot}NaF$ forms a solid solution in which fluoride is replaced by chloride to a limited extent.

No indication of the mineral sulfohalite $2Na_2SO_4{\cdot}NaF{\cdot}NaCl$ has been obtained at these temperatures.

A graphic method has been developed to show the relation of the composition of anhydrous solid phases to the solutions in equilibrium with such phases in quaternary systems composed of water with three salts containing a common ion.

New optical and crystallographic data are recorded for the compound $Na_2SO_4{\cdot}NaF$.

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[4] Penfield, *Am. J. Sci.*, **9**, 425 (1900).

[5] Gale and Hicks, *ibid.*, **38**, 273 (1914).

[6] Teeple, *Ind. Eng. Chem.*, **13**, 249 (1921).