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THE SYSTEM Na_2SO_4–NaF–NaCl–H_2O. I. THE TERNARY SYSTEMS WITH WATER AND TWO SALTS[1]

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Before investigating equilibrium relations in the quaternary system Na_2SO_4–NaF–NaCl–H_2O, it was necessary to determine first these relations in each of the three ternary systems of two salts and water. The data for the ternary systems are given here and the data for the quaternary system will be published in Part II.

Sodium sulfate and sodium chloride were purified by the usual methods. Sodium fluoride forms an acid fluoride in the presence of only a small excess of hydrofluoric acid.[2] To obtain pure sodium fluoride, recrystallized sodium carbonate was dissolved in a small volume of water and neutralized with the smallest possible excess of hydrofluoric acid. After warming to remove carbon dioxide, the solution was cooled and the precipitated sodium fluoride filtered and washed with alcohol. An analysis by conversion to the sulfate and an optical examination with the petrographic microscope checked its purity.

For the determination of solubility isotherms appropriate mixtures of salts and water were placed in hard rubber bottles and shaken at constant temperature in a water thermostat for at least twenty-four hours. A check upon the attainment of equilibrium was made by running duplicate determinations held at constant temperature for longer periods of time. Solutions for analysis were removed through filters of glass wool directly into weighing tubes. Depending on the solid phases present and whether a wet or dry residue was desired, different procedures were followed. The solid phases, or "residues," which were in equilibrium with the solutions, were either pressed between filter papers until dry, or washed quickly with alcohol on a Gooch crucible and then dried between filter papers. Both methods have disadvantages, and in general it is not possible to obtain the composition of the residues as accurately as that of the solutions. In some cases wet residues were analyzed and the composition of the solids determined by the graphic method of Schreinemakers.[3]

In the analysis of solutions and solids, sodium chloride was determined by titration with silver nitrate solution, using potassium chromate as the indicator. The determination of sulfate as $BaSO_4$ is entirely unreliable in

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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] Jehu and Hudleston, *J. Chem. Soc.*, **125**, 1451–1456 (1924).

[3] Schreinemakers, *Z. physik. Chem.*, **43**, 307 (1903).

the presence of fluorides. Sodium fluoride was determined by converting the salts to sodium sulfate with sulfuric acid and igniting in a current of air containing ammonia, and sodium sulfate determined by difference. On account of the considerable difference between the equivalent weights of sodium fluoride and sodium sulfate, this method of indirect analysis is much more accurate than is commonly the case with indirect methods. The formula used in calculating the weight of sodium fluoride is: $x = 1.4468 (b - a) - 0.3113\, c$, in which a, b and c represent, respectively, the weight of mixed salts, the weight of sodium sulfate after the conversion of chlorides and fluorides to sulfate, and the weight of sodium chloride.

Eutectic points with ice as one of the solid phases were determined in a small vacuum-jacketed flask, by shaking a mixture of wet crushed ice with an excess of the salt or salts in question. After removal of a sample of the solution for analysis, more of each solid phase was added and the temperature again observed. The thermometers were calibrated with care and the eutectic temperatures are probably in error by not more than 0.1°. Transition temperatures were determined by the same general method as eutectic temperatures.

The System Na_2SO_4–NaF–H_2O.—In the system Na_2SO_4–NaF–H_2O a double salt $Na_2SO_4 \cdot NaF$ forms. Wolters[4] found this double salt at high temperatures in his investigation of the fusion relations in the ternary system Na_2SO_4–NaF–NaCl. Below a transition temperature (17.5°) the double salt breaks down into sodium fluoride and the decahydrate of sodium sulfate. Above the transition temperature of sodium sulfate (32.38°), a solubility isotherm consists of three branches meeting in two univariant points at which two solid phases (sodium fluoride and double salt or sodium sulfate and double salt) are in equilibrium. The transition temperature of sodium sulfate decahydrate in the presence of the double salt (32.36°) is almost identical with that of the pure decahydrate, on account of the slight solubility of sodium fluoride. Between 32.36° and the transition point of the double salt (17.5°), a solubility isotherm consists of three branches, with sodium sulfate present as the decahydrate. Below 17.5°, an isotherm consists of two branches meeting at a point where the two single salts coexist as solid phases. The solubility data obtained at four temperatures are given in Table I. Where less than 0.1% of a salt was found in solution it is reported as a trace (tr.).

The solid phases present in the residue were determined in the usual manner by plotting the composition of solutions and residues on an equilateral triangle. The nature of the solid phases was checked by an examination with the petrographic microscope. The identity of the solid phase or phases in equilibrium with a given solution is noted in Table I. Ds indicates the double salt $Na_2SO_4 \cdot NaF$.

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[4] Wolters, *Neues Jahrb. Mineral. Geol. Beil.*, 30, 55–96 (1910).

TABLE I

SOLUBILITY ISOTHERMS—SYSTEM Na_2SO_4–NaF–H_2O

Solution,		Residue,		
% Na_2SO_4	% NaF	% Na_2SO_4	% NaF	Solid phases
		$T = 35°$		
32.97	None			Na_2SO_4
32.96	None			Na_2SO_4
32.87	Tr.	95.43	4.57	Na_2SO_4 and Ds[b]
32.75	0.13	87.97	12.03	Na_2SO_4 and Ds
32.79	Tr.	82.35	17.65	Na_2SO_4 and Ds
18.11	0.62	64.57	18.51[a]	Ds[b]
11.60	1.57	77.23	22.77	Ds
9.58	2.09	75.68	24.32	Ds
8.51	2.45	65.48	34.52	Ds and NaF
8.73	2.54	8.43	91.56	Ds and NaF
4.34	3.18	1.61	74.18[a]	NaF
None	4.02			NaF
None	3.97			NaF
		$T = 25°$		
21.71	None			$Na_2SO_4 \cdot 10H_2O$
21.71	None			$Na_2SO_4 \cdot 10H_2O$
21.25	0.42	43.93	1.40[a]	$Na_2SO_4 \cdot 10H_2O$ and Ds
21.43	0.33	55.91	13.17[a]	$Na_2SO_4 \cdot 10H_2O$ and Ds
11.48	1.74	76.75	23.25	Ds
8.86	2.37	46.88	28.89[a]	Ds and NaF
8.48	2.34	14.49	43.60[a]	Ds and NaF
4.48	3.13	2.17	57.79[a]	NaF
None	3.98			NaF
None	3.97			NaF
		$T = 15°$		
11.72	None			$Na_2SO_4 \cdot 10H_2O$
11.67	None			$Na_2SO_4 \cdot 10H_2O$
9.48	2.51	39.07	3.94[a]	$Na_2SO_4 \cdot 10H_2O$ and NaF
9.51	2.48	11.88	69.50[a]	$Na_2SO_4 \cdot 10H_2O$ and NaF
None	3.93			NaF
None	3.92			NaF
		$T = 10°$		
8.31	None			$Na_2SO_4 \cdot 10H_2O$
8.38	None			$Na_2SO_4 \cdot 10H_2O$
6.41	2.92	13.25	53.14[a]	$Na_2SO_4 \cdot 10H_2O$ and NaF
6.37	3.04	36.59	4.21[a]	$Na_2SO_4 \cdot 10H_2O$ and NaF
3.95	3.20	1.96	55.53[a]	NaF
None	3.92			NaF
None	3.97			NaF

[a] Wet residue analyzed. [b] Ds = $Na_2SO_4 \cdot NaF$ (double salt).

The data for eutectic and transition temperatures are given in Table II. The two eutectics with ice and a single salt have been determined before.[5]

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[5] Guthrie, *Phil. Mag.*, **6**, 40 (1878); De Coppet, *Z. physik. Chem.*, **22**, 239 (1897); Chretien, *Caliche*, **9**, 248 (1927).

The transition point where the solid phases are $Na_2SO_4 \cdot 10H_2O$, NaF and $Na_2SO_4 \cdot NaF$ is somewhat difficult to obtain. Solubility isotherms indicated that this transition temperature was between 15 and 25°. A mixture of sodium fluoride, decahydrate of sodium sulfate and a small amount of the double salt $Na_2SO_4 \cdot NaF$ and water was placed in a vacuum flask at 21° and the temperature observed. The temperature slowly dropped, finally remaining constant for several hours. The reverse of this determination, starting below the transition temperature, did not give a sharp result.

TABLE II

EUTECTIC AND TRANSITION TEMPERATURES—SYSTEM Na_2SO_4–NaF–H_2O

Solid phases	Temp., °C.	Solution % Na_2SO_4	Solution % NaF	Corresponding point in the diagram (Fig. 1)
Ice + NaF	−3.02	None	4.02	A
Ice + NaF	−2.98	None	3.82	A
Ice + $Na_2SO_4 \cdot 10H_2O$	−1.11	3.97	None	B
Ice + $Na_2SO_4 \cdot 10H_2O$	−1.14	4.11	None	B
Ice + NaF + $Na_2SO_4 \cdot 10H_2O$	−3.08	1.65	3.60	C
Ice + NaF + $Na_2SO_4 \cdot 10H_2O$	−3.08	1.70	3.34	C
Ice + NaF + $Na_2SO_4 \cdot 10H_2O$	−3.00	1.68	3.33	C
$Na_2SO_4 \cdot 10H_2O$ + NaF + Ds	17.45	12.54	2.00	D
$Na_2SO_4 \cdot 10H_2O$ + NaF + Ds	17.50	12.63	1.83	D
$Na_2SO_4 \cdot 10H_2O$ + Na_2SO_4[a]	32.383[a]	33.24[b]	None	E
$Na_2SO_4 \cdot 10H_2O$ + Na_2SO_4 + Ds	32.36	33.16	Tr	F
$Na_2SO_4 \cdot 10H_2O$ + Na_2SO_4 + Ds	32.36	33.06	Tr.	F

[a] "International Critical Tables," 1926, Vol. I, p. 66. [b] *Ibid.*, 1928, Vol. III, p. 371.

These data cannot be properly shown as a projection on a triangular base. The results are, therefore, represented in a space figure (Fig. 1),

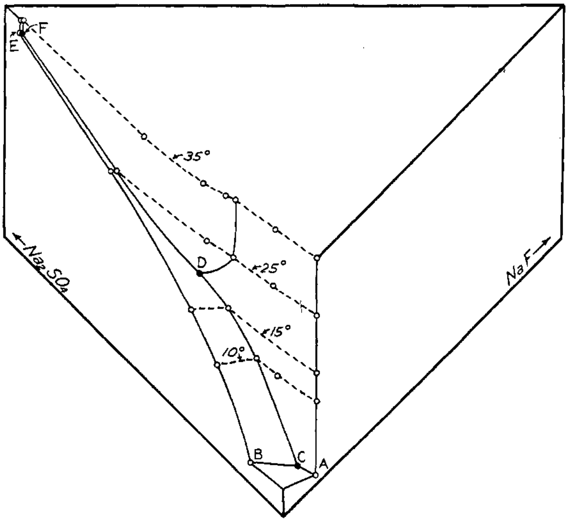

Fig. 1.—System Na_2SO_4–NaF–H_2O. Space model.

plotting temperatures vertically from a triangular base. The eutectic and transition temperatures (Fig. 1) are lettered to correspond with the data in Table II. Solubility isotherms are represented as dotted lines. The results given in the tables for invariant and univariant points have been averaged for representation in Fig. 1.

The Double Salt $Na_2SO_4 \cdot NaF$.—The double salt $Na_2SO_4 \cdot NaF$ was first described by Marignac[6] who obtained it by evaporation of the mother liquor from a preparation of sodium fluoride with hydrofluoric acid containing some sulfuric acid. He describes it as occurring in hexagonal plates twinned parallel to the base. The crystals were a combination of the base and four rhombohedrons. The crystals gave poor signals on the goniometer. Marignac assigns the crystals with some doubt to the rhombohedral class of the hexagonal system.

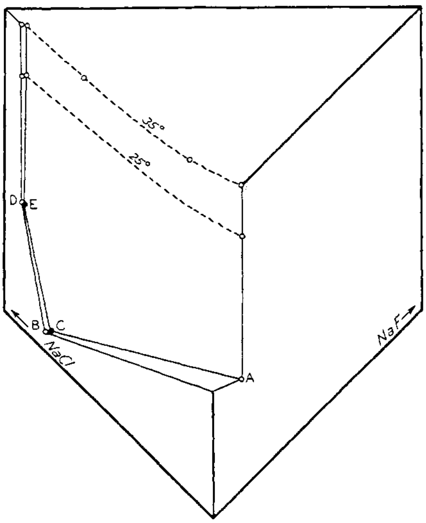

Fig. 2.—System $NaF-NaCl-H_2O$. Space model.

Wolters[7] prepared the double salt from water solution at 35° and claims that it is pseudo-hexagonal up to 105° (±2°), where it becomes hexagonal. This transition temperature is above the range of temperatures studied by us.

Crystals of the double salt were prepared by isothermal evaporation at 35°. Five crystals were measured on a two circle goniometer. The crystals appeared bright and sharp but did not give good signals. The crystals are tabular with hexagonal outline and decided trigonal symmetry. The base is rough and the other faces, although very definite, usually gave many goniometric signals in the zone with the base. Twinning on the base is common. The results of our measurements on five crystals give

$$c = 1.77$$

$$(0001) \wedge (10\bar{1}1) = 63.9°; \quad (0001) \wedge (01\bar{1}2) = 45.7°$$

$$(0001) \wedge (03\bar{3}2) = 72.0°$$

The double salt $Na_2SO_4.NaF$ is uniaxial, optically positive, $\epsilon_{Na} = 1.439$, $\omega_{Na} = 1.436$ with a cleavage parallel to (0001).

The System $NaF-NaCl-H_2O$.—The solubility isotherms at 25 and 35°, taken in connection with the composition of the residues, show that no double salt forms and that solid solution, if present, is too slight to be

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[6] Marignac, *Annales des Mines*, **15**, 236 (1859).

[7] Ref. 4.

detected. The transition temperature of sodium chloride dihydrate has been determined repeatedly by others, though the results in the literature do not agree closely. We found it sharp and easily obtained. Sodium fluoride lowers this transition temperature but slightly on account of its slight solubility in the presence of sodium chloride.

The results obtained are given in Tables III and IV and are represented in Fig. 2.

TABLE III

SOLUBILITY ISOTHERMS—SYSTEM $NaCl-NaF-H_2O$

Solution		Residue		
% NaCl	% NaF	% NaCl	% NaF	Solid phases
		T = 35°		
26.63	None			NaCl
26.61	None			NaCl
26.18	0.34	74.77	25.23	NaCl and NaF
26.13	0.29	23.85	76.15	NaCl and NaF
18.43	0.54	4.58	75.98[a]	NaF
5.41	2.38	1.58	72.94[a]	NaF
None	4.02			NaF
None	3.97			NaF
		T = 25°		
26.43	None			NaCl
26.38	None			NaCl
26.12	0.31	56.50	25.91[a]	NaCl and NaF
26.24	.12	19.58	42.06[a]	NaCl and NaF
None	3.98			NaF
None	3.97			NaF

[a] Wet residue analyzed.

TABLE IV

EUTECTIC AND TRANSITION TEMPERATURES—SYSTEM $NaCl-NaF-H_2O$

Solid phases	Temp., °C.	Solution		Corresponding point in diagram (Fig. 2)
		% NaCl	% NaF	
Ice + NaF	− 3.02	None	4.02	A
Ice + NaF	− 2.98	None	3.82	A
Ice + $NaCl\cdot 2H_2O$	−20.94	23.18	None	B
Ice + $NaCl\cdot 2H_2O$ + NaF	−21.19	23.69[a]	0.24	C
$NaCl\cdot 2H_2O$ + NaCl	+ 0.08	26.39	None	D
$NaCl\cdot 2H_2O$ + NaCl	.10	26.53	None	D
$NaCl\cdot 2H_2O$ + NaCl + NaF	− .06	26.25	0.19	E

[a] This result is probably somewhat too high.

The System $Na_2SO_4-NaCl-H_2O$.—This system has been investigated previously by Meyerhoffer and Saunders,[8] Seidell[9] and Blasdale.[10] We have determined the points necessary for use in the four-component sys-

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[8] Meyerhoffer and Saunders, *Z. physik. Chem.*, **28**, 453 (1899).

[9] Seidell, *Am. Chem. J.*, **27**, 55 (1902).

[10] Blasdale, *Ind. Eng. Chem.*, **10**, 344 (1918).

tem. So far as they are comparable, our results check closely with those of Blasdale.

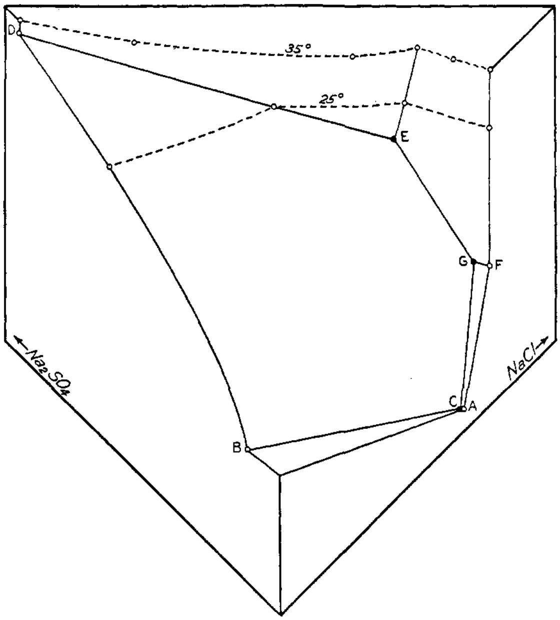

Fig. 3.—System Na_2SO_4–NaCl–H_2O. Space model.

The results obtained are given in Tables V and VI and are plotted in Fig. 3 in the same manner as the preceding ternary systems.

TABLE V

SOLUBILITY ISOTHERMS—SYSTEM Na_2SO_4–NaCl–H_2O

Solution		Residue		
% Na_2SO_4	% NaCl	% Na_2SO_4	% NaCl	Solid phases
		T = 35°		
32.97	None			Na_2SO_4
32.96	None			Na_2SO_4
24.43	5.86	100.00	None	Na_2SO_4
9.78	18.61	98.67	1.33[a]	Na_2SO_4
6.00	23.43	75.50	24.50	Na_2SO_4 and NaCl
6.17	23.39	20.78	79.22	Na_2SO_4 and NaCl
6.11	23.41	1.77	98.23	Na_2SO_4 and NaCl
3.00	25.01	None	100.00	NaCl
None	26.63			NaCl
None	26.61			NaCl
		T = 25°		
21.71	None			$Na_2SO_4 \cdot 10H_2O$
21.71	None			$Na_2SO_4 \cdot 10H_2O$
14.98	14.15	78.25	1.94[b]	$Na_2SO_4 \cdot 10H_2O$ and Na_2SO_4
15.01	14.06	65.58	1.65[b]	$Na_2SO_4 \cdot 10H_2O$ and Na_2SO_4

TABLE V (*Concluded*)

Solution		Residue		
% Na_2SO_4	% NaCl	% Na_2SO_4	% NaCl	Solid phases
14.91	14.10	64.70	1.68[b]	$Na_2SO_4 \cdot 10H_2O$ and Na_2SO_4
14.84	14.17	46.39	2.29[b]	$Na_2SO_4 \cdot 10H_2O$ and Na_2SO_4
6.91	22.78	72.84	16.21[b]	Na_2SO_4 and NaCl
6.92	22.76	12.61	72.54[b]	Na_2SO_4 and NaCl
None	26.63			NaCl
None	26.61			NaCl

[a] This residue was contaminated with sodium chloride from the solution. [b] Wet residue.

TABLE VI

EUTECTIC AND TRANSITION TEMPERATURES—SYSTEM Na_2SO_4–NaCl–H_2O

Solid phases	Temp., °C.	Solution % Na_2SO_4	Solution % NaCl	Corresponding point in diagram (Fig. 3)
Ice + $NaCl \cdot 2H_2O$	−20.94	None	23.18	A
Ice + $Na_2SO_4 \cdot 10H_2O$	− 1.11	3.97	None	B
Ice + $Na_2SO_4 \cdot 10H_2O$	− 1.14	4.11	None	B
Ice + $Na_2SO_4 \cdot 10H_2O$ + $NaCl \cdot 2H_2O$	−21.32	0.31	23.43	C
Na_2SO_4 + $Na_2SO_4 \cdot 10H_2O$[a]	32.383[a]	33.24[b]	None	D
Na_2SO_4 + $Na_2SO_4 \cdot 10H_2O$ + NaCl	17.90	7.77	22.31	E
$NaCl \cdot 2H_2O$ + NaCl	+ 0.08	None	26.39	F
$NaCl \cdot 2H_2O$ + NaCl	+ .10	None	26.53	F
$NaCl \cdot 2H_2O$ + NaCl + $Na_2SO_4 \cdot 10H_2O$	.0	1.32	25.79	G

[a] "International Critical Tables," 1926, Vol. I, p. 66. [b] *Ibid.*, 1928, Vol. III, p. 371.

Summary

Solubility determinations were made on the ternary system Na_2SO_4–NaF–H_2O at 35, 25, 15 and 10°, and on the ternary systems NaF–NaCl–H_2O and Na_2SO_4–NaCl–H_2O at 35 and 25°. The necessary eutectics and transition temperatures were determined to define each ternary system between its ternary eutectic and 35°. These data are presented by tables and graphically by space models.

The nature and identity of the various solid phases was checked with the petrographic microscope. The crystallographic and optical properties of the double salt $Na_2SO_4 \cdot NaF$ were measured.

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