CXVIII.—*The Ternary System Sodium Sulphide–Sodium Sulphate–Water.*

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THE fact that anhydrous sodium sulphite and sulphate, and their corresponding hydrates, crystallise together within limits (Rivett and Lewis, *Rec. trav. chim.*, 1923, **42**, 954; J., 1924, **125**, 1156, 1162) suggested an inquiry into the relations between sodium sulphide and sodium sulphate. This has been carried out at each of the five temperatures 0·1°, 18°, 25°, 31° and 40°, the complete ternary system being described in each case.

For the most part the salts used have been of analytical reagent (B.D.H.) standard. Mixtures of these and water in varying amounts have been brought to equilibrium in rubber-stoppered glass tubes, the proportions taken being such that about 6% of the total was present as solid when equilibrium was attained. Three methods of attaining equilibrium were employed: (i) cooling homogeneous solutions from higher temperatures, inoculating, if necessary, with the appropriate solid phase (systems at 0·1° and 18°) : (ii) heating heterogeneous mixtures from lower temperatures (systems at 25° and 31°) : (iii) evaporating homogeneous solutions under reduced pressure at the temperature of experiment until sufficient solid appeared (system at 40°). When all phases were present, the tubes were mechanically rotated in a thermostat for from 4 to 40 hours.

The second method is satisfactory in giving the course only of the solution curves : it will not give accurate information as to compositions of solid phases, but it sufficed in the cases where it was used. The third method was carried out in tubes fitted with vertical side limbs and connected in batches of six with a small cooled receiver exhausted to about 40 mm. pressure. The tubes were clamped horizontally to a tilting platform in the bath and were gently rocked during the evaporation, which generally occupied about 3 hours. In order to avoid possible loss of hydrogen sulphide, the mixtures were kept in connexion with the pump for as short a time as possible, the vacuum being maintained by condensation. The distillate from six tubes was collected and tested for sulphide. The amount found, part of which was due to priming, was insufficient to affect the analyses appreciably. When sufficient solid had separated, the vacuum was broken and the rocking continued for from 2 to 12 hours.

On attainment of equilibrium, a sample of the solution was withdrawn in a pipette (suitably heated or cooled) through a cotton-wool plug, and weighed. Densities so obtained are correct to one or two units in the third decimal place. Dilution to an appropriate extent gave the solution which was analysed. The moist solid was obtained by rapid filtration on a Büchner funnel and a weighed amount was dissolved to a known volume. In some cases, the wet solid was washed with alcohol and dried between folds of blotting paper. In analysis, sulphide was determined by titration against standard acid, with phenolphthalein as indicator, and sulphate was determined gravimetrically as barium sulphate.

Discussion of Results.

The experimental results are given in Tables I to VI. Compositions are expressed in % of anhydrous salt by weight. In the last column, mixed crystals are indicated by M.C. followed by the formula of the major constituent.

The first point to be noted is that at 0° sodium sulphide has been obtained as a decahydrate, a form apparently not hitherto described. Analysis of the solid, after washing with alcohol and drying with blotting paper, gave Na_2S, 30·04% : $Na_2S,10H_2O$ requires 30·23 and $Na_2S,9H_2O$ requires 32·49%. In the ternary system at 0·1° the

TABLE I.

Isotherm at 0·1°.

	Solutions.		Wet solids.		
	% by weight.		% by weight.		
$D^{0^\circ}_{4^\circ}$.	Na_2S.	Na_2SO_4.	Na_2S.	Na_2SO_4.	Solid phases.
1·122	11·33	—	30·0	—	M.C. $Na_2S,10H_2O$.
1·125	11·34	0·63	23·4	0·12	
—	11·22	0·93	23·1	0·43	
1·137	11·94	1·16	—	—	
1·131	11·21	1·23	29·6	0·96	M.C. $Na_2S,10H_2O$ and M.C. $Na_2SO_4,10H_2O$.
1·130	11·14	1·25	25·1	7·30	
1·131	11·23	1·19	21·1	13·54	
1·129	11·16	1·16	18·49	16·53	
1·129	11·18	1·23	18·34	16·53	
1·132	11·23	1·18	14·49	21·0	
1·129	11·11	1·19	0·47	43·2	M.C. $Na_2SO_4,10H_2O$.
1·124	10·77	1·24	5·56	23·6	
1·110	9·49	1·27	4·49	24·2	
1·099	8·32	1·28	2·59	33·5	
1·091	7·36	1·48	3·60	23·6	
1·081	6·16	1·54	2·48	28·9	
1·066	4·79	1·68	1·64	30·6	
1·052	3·16	2·11	1·49	27·5	
1·041	1·44	2·99	0·45	32·5	

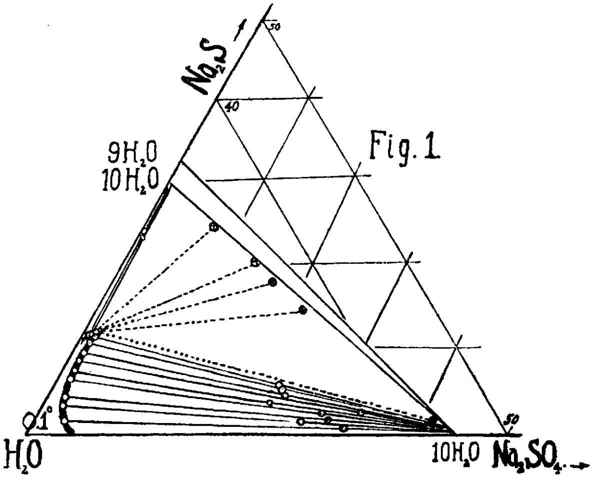


Fig. 1

Isotherm at 0·1°.

solution curve for this decahydrate is short (see Fig. 1), but there is definite indication of the separation of mixed crystals containing a very little $Na_2SO_4,10H_2O$.

At the sodium sulphate end the mixed-crystal formation is greater, the limiting member of the series containing 42% of sulphate and 1·5% of sulphide. The points in Fig. 1 marked by crosses within circles represent mixtures of two solid phases in equilibrium with the solution at the intersection of the two solution curves. The solids were obtained almost free from mother-liquor by washing with alcohol and drying with blotting paper. It will be seen that they all lie very near to the line joining the end corresponding to mixed crystals of (mainly) $Na_2SO_4,10H_2O$ containing sulphide and the point representing the composition $Na_2S,10H_2O$. This gives independent proof of the existence of a decahydrate of the sulphide.

Between it and the nonahydrate in the binary system the transition point has been shown by the cooling method to be 4·7°, the saturated solution then containing 12·46% of sodium sulphide and having a density of 1·128.

TABLE II.

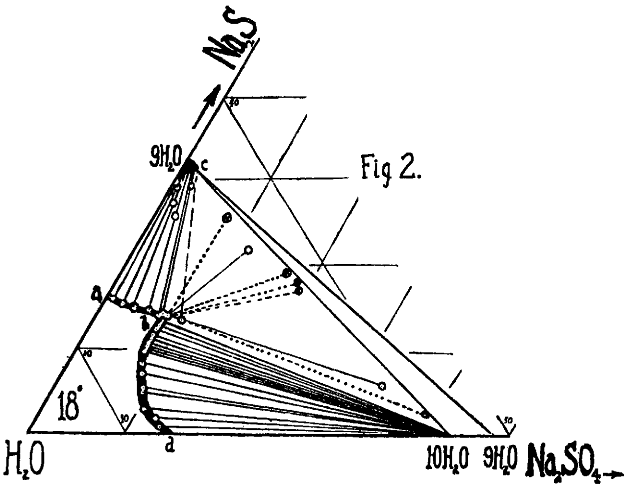
Isotherm at 18°.

	Solutions.		Wet solids.		
	% by weight.		% by weight.		
D^{t}_{4}.	Na_2S.	Na_2SO_4.	Na_2S.	Na_2SO_4.	Solid phases.
1·169	15·95	—	—	—	$Na_2S,9H_2O$.
—	15·65	0·53	30·40	0·32	M.C. $Na_2S,9H_2O$.
—	15·33	2·28	29·27	0·63	
1·187	15·08	3·47	28·15	1·11	
1·197	14·50	5·20	25·96	2·13	
1·212	14·02	5·83	31·56	0·74	
—	13·98	6·44	30·10	1·66	
—	—	—	25·56	7·61	M.C. $Na_2S,9H_2O$ and $Na_2SO_4,10H_2O$.
1·212	13·90	7·21	22·23	11·91	
—	—	—	19·31	17·54	
1·210	13·95	7·24	18·38	18·91	
—	—	—	16·93	19·49	
1·205	13·84	7·22	5·12	33·99	
1·210	13·98	7·23	2·56	40·28	
—	13·78	7·16	0·65	42·91	
1·225	13·15	9·75	31·50]	1·75	
1·208	13·08	7·01	4·12	32·11	$Na_2SO_4,10H_2O$.
1·195	12·46	7·00	2·93	35·21	
1·186	12·14	6·93	3·62	32·98	
1·180	11·16	6·79	—	—	
1·175	10·91	6·96	2·08	37·68	
1·169	10·33	7·19	2·35	35·61	
1·167	10·04	7·17	3·13	32·89	
1·165	9·96	7·09	1·04	40·70	
1·162	9·47	7·15	2·20	35·82	
1·149	7·99	7·64	1·82	35·84	
1·143	6·82	8·09	1·88	33·39	
1·132	5·33	9·05	1·32	34·65	
1·130	4·54	9·30	0·93	36·79	
1·131	2·84	10·67	0·54	37·27	
1·126	1·51	11·91	0·37	36·05	
1·126	0·62	13·31	0·15	36·17	

At 18° (Table II) the solid separating at the sulphide end is the ordinary nonahydrate containing some dissolved sulphate (see

Fig. 2). Whether the latter is there with water in the same molecular proportion of 1 : 9 cannot be stated. At the sulphate end, however, there is no indication of any appreciable solubility of sodium sulphide in $Na_2SO_4,10H_2O$. It would seem that $Na_2S,10H_2O$ cannot exist in mixed crystals at 18°, while the nonahydrate of the sulphide is insoluble in the decahydrate of the sulphate.

There is no appreciable mixed-crystal formation at 25° or 31° (Tables III and IV) either in the hydrated or anhydrous sulphate



Isotherm at 18°.

TABLE III.

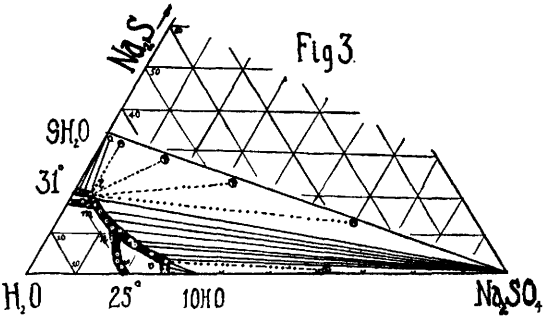
Isotherm at 25°.

	Solutions.		Wet solids.		
	% by weight.		% by weight.		Solid phases.
$D^{t°}_{4°}$.	Na_2S.	Na_2SO_4.	Na_2S.	Na_2SO_4.	
1·183	17·86	—	31·68	—	$Na_2S,9H_2O$.
1·202	17·17	3·40	31·73	0·27	
1·205	16·61	5·01	31·76	—	
1·229	15·84	7·18	27·73	13·10	$Na_2S,9H_2O$ and Na_2SO_4.
1·224	15·89	6·87	23·43	25·89	
1·221	16·07	6·32	14·35	46·86	
1·228	14·68	8·06	2·58	79·29	Na_2SO_4.
1·222	12·68	10·80	0·61	93·18	
1·237	11·21	12·56	0·13	96·78	
1·241	10·04	14·51	0·99	90·79	
1·240	9·96	14·70	0·57	65·25	Na_2SO_4 and $Na_2SO_4,10H_2O$.
1·241	9·96	14·67	0·44	48·28	
1·204	4·40	17·12	0·35	40·98	$Na_2SO_4,10H_2O$.
1·203	3·27	17·84	0·49	37·76	
—	1·63	19·71	0·47	35·80	

TABLE IV.

Isotherm at 31°.

	Solutions.		Wet solids.		
	% by weight.		% by weight.		
$D'_{4°}$	Na_2S.	Na_2SO_4.	Na_2S.	Na_2SO_4.	Solid phases.
1·202	20·60	—	31·42	—	$Na_2S,9H_2O$.
1·210	20·44	1·05	32·44	0·05	
—	19·57	3·04	29·64	0·87	
1·213	19·46	4·11	31·26	1·77	$Na_2S,9H_2O$ and Na_2SO_4.
—	19·66	4·41	30·41	5·47	
1·229	19·33	4·04	27·41	14·89	
1·222	19·69	4·32	20·39	35·73	
1·228	19·42	4·20	11·47	63·46	
1·253	22·22	2·56	3·01	86·41	Na_2SO_4.
1·214	18·69	4·79	3·57	82·00	
—	16·36	6·58	3·59	79·98	
1·214	14·39	8·59	2·19	86·79	
1·219	12·14	11·56	1·96	88·01	
1·228	9·83	14·46	1·27	89·72	
—	7·47	18·92	0·45	92·39	
1·248	6·97	19·47	1·37	85·68	
1·264	4·81	23·06	1·99	68·91	
1·288	2·85	27·39	0·34	84·30	Na_2SO_4 and $Na_2SO_4,10H_2O$.
1·290	2·31	28·65	0·15	64·25	
1·291	2·43	28·72	0·25	42·85	$Na_2SO_4,10H_2O$.
1·294	1·47	29·15	0·27	41·88	
1·285	0·40	29·97	0·05	41·81	



Isotherms at 25° *and* 31°.

solid phase. The relations are shown in Fig. 3 and need no discussion. At 40°, where only anhydrous sulphate can exist, there is again no discernible miscibility. At all three temperatures, the part of the system in which solid sulphide appears is so small that one cannot make definite assertions about the solid phase.

By the determination of temperature–time curves in slow cooling and heating of suitably chosen mixtures, the transition points were determined as set out in Table VI, together with the compositions of saturated solutions in equilibrium with the solids indicated in the

TABLE V.

Isotherm at 40°.

Solutions.			Wet solids.		
	% by weight.		% by weight.		
$D^{t^\circ}_{4^\circ}$.	Na_2S.	Na_2SO_4.	Na_2S.	Na_2SO_4.	Solid phases.
1·248	25·09	—	31·04	—	$Na_2S,9H_2O$.
1·248	25·01	—	32·23	—	
1·238	24·06	0·49	32·37	trace	
1·238	23·93	0·88	32·94	0·05	
1·256	24·28	1·62	32·08	1·58	$Na_2S,9H_2O$ and Na_2SO_4.
—	23·44	1·77	31·75	2·96	
1·248	23·72	1·90	31·25	5·63	
1·247	23·79	1·84	30·53	6·69	
1·253	23·62	1·90	27·57	16·59	
1·253	23·57	1·84	2·08	91·46	Na_2SO_4.
1·241	23·25	1·79	1·69	93·25	
1·223	23·04	1·91	1·89	48·98	
—	22·30	1·94	3·04	86·67	
1·233	21·91	2·44	—	—	
1·233	21·99	2·45	2·39	87·39	
1·239	21·27	2·79	4·14	81·48	
1·228	20·91	3·04	2·28	89·18	
1·233	20·36	3·41	1·76	91·62	
—	14·08	25·22	0·78	95·43	
1·223	15·45	6·53	—	—	
—	14·97	7·37	1·90	89·62	
1·223	14·25	8·72	3·33	75·75	
1·220	14·31	8·17	—	—	
1·236	9·78	14·14	2·07	81·18	
—	9·49	15·23	1·89	82·58	
1·260	6·18	20·25	1·83	75·63	
—	3·56	24·43	0·78	80·90	
1·302	1·32	28·90	0·18	83·71	

TABLE VI.

Transition points.

Transition.	Temp.	% by weight in soln.		
		Na_2S.	Na_2SO_4.	$D^{t^\circ}_{4}$.
Binary.				
$Na_2S,10H_2O \leftrightarrows Na_2S,9H_2O$.	4·7° (h) 4·7 (c).	12·46	—	1·128
Ternary.				
Same in satd. Na_2SO_4.	2·3 (h) 2·3 (c)	11·49	1·40	1·135
Ternary.				
$Na_2SO_4,10H_2O \leftrightarrows Na_2SO_4$ in satd. Na_2S.	20·9 (h) 20·2 (c)	13·41	9·48	—
? —	29·6 (h) 29·6 (c)	19·97	4·48	1·331

(h) = arrest on heating. (c) = arrest on cooling.

first column. Sulphate lowers the transition point between deca- and nona-hydrates of the sulphide from 4·7° to 2·3°, whilst the transition point between decahydrated and anhydrous sulphates may be reduced by sulphide from 32·4° to 20·6°. For small concentrations of sodium sulphide, the depression of this transition point has been measured and found to be directly proportional to the concentration of sulphide. It may be expressed by $D = 0{\cdot}625C$, where D is the depression and C the concentration of sulphide in g. per 100 g. of solution.

A curious arrest at 29·6° (Table VI) has not been explained. The solution has a high density and the arrest may correspond with the formation of a metastable hydrate no trace of which was found in the work on the 31°-isotherm.

Summary.

1. The system sodium sulphide–sulphate–water has been investigated between 0·1° and 40°.

2. Sodium sulphide has been found to form a decahydrate which has not been previously described. The transition point in the binary system between deca- and nona-hydrates is 4·7°.

3. Mutual miscibility is shown by the solid decahydrates of sulphide and sulphate at 0·1°.

4. At 18°, $Na_2S,9H_2O$ can dissolve sulphate (as nonahydrate ?) but neither $Na_2SO_4,10H_2O$ nor Na_2SO_4 shows appreciable tendency to include sulphide in its crystals.

5. The transition point between deca- and nona-hydrated sulphides is lowered in the ternary system by sulphate to 2·3°; while that between decahydrated and anhydrous sulphate is lowered by sulphide to 20·6°.

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