CXVII.—*The Ternary System Sodium Thiosulphate–Sodium Sulphate–Water.*

By Richard Randolph Garran.

The system sodium thiosulphate–sodium sulphate–water has been examined at 0·8°, 18°, 25° and 40°, the temperature being maintained constant to within 0·02° in the last three cases and to within 0·1° in the first. The transition between decahydrated and anhydrous sodium sulphate in presence of sodium thiosulphate has also been studied.

Mixtures, prepared as indicated in the descriptions of the various isotherms, were rotated in stoppered glass tubes in a thermostat for periods varying from 3 to 24 hours; then, after allowing the solid to settle, a definite volume of solution was drawn off by means of a pipette fitted with a cotton-wool filter and weighed in a tared bottle; the solid was rapidly drained on a Büchner funnel and a portion of it weighed. The solution was diluted and the solid dissolved to known volumes in each case and aliquot parts of these were taken for analysis. The values of the densities of the solutions are probably not accurate beyond two or three units in the third decimal place.

Thiosulphate was determined by adding a known small excess of standard iodine solution and titrating this excess with a solution of sodium thiosulphate the normality of which was obtained from a hydrochloric acid solution (standardised against calc-spar) by means of a mixture of potassium iodide and iodate.

For the determination of the sulphate, the following methods were decided upon after many trials:

(i) The solution was evaporated to dryness with excess of sulphuric acid, and the residue heated to convert it completely into sulphate and to drive off the excess of acid and the sulphur which was formed. From the total weight of sulphate present and the known amount of thiosulphate, the amount of sulphate originally present was readily calculated.

(ii) The solution of thiosulphate was oxidised, by heating with bromine water in the presence of a little alkali, in accordance with the following equation (Mayr and Peyfuss, *Z. anorg. Chem.*, 1923,

127, 123; 1924, **131**, 203): $Na_2S_2O_3 + 4Br_2 + 5H_2O = Na_2SO_4 + H_2SO_4 + 8HBr$. After the excess of bromine had been expelled, the sulphate was precipitated as barium sulphate and the amount of sodium sulphate originally present calculated as above.

(iii) When thiosulphate was present in large excess, method (ii) was found to be untrustworthy. The sulphate present was then precipitated as barium sulphate in cold neutral solution (barium thiosulphate is soluble under these conditions), allowed to settle for 24 hours, and washed three times by decantation, being allowed to settle during 18 to 24 hours each time. The precipitate was then boiled with dilute hydrochloric acid to make it coarser, filtered off, and weighed. This method was found to be trustworthy, but the time required was considerable.

The isotherms at 0·8° and 25° are based entirely on analyses by the first method: that at 18° almost entirely, and that at 40° partly, on the second and third methods. Compositions are expressed as percentages of components by weight, and mixed crystals are indicated in the tables by *M.C.* followed by the formula of the major constituent.

Discussion of Results.

The results obtained at 0·8° and 18° are shown in Tables I and II and are plotted in the usual triangular diagram in Fig. 1. Only the solution curves at 0·8° are shown, as the two systems are of similar general form. Suitable mixtures were prepared from water, pure (A.R.) crystals of sodium thiosulphate pentahydrate and pure commercial (B.D.H.) crystals of sodium sulphate decahydrate, and heated to homogeneity in stoppered tubes which were then rotated in a thermostat for several hours (generally over-night) after the solid had settled out. In a few cases, in solutions containing a preponderance of thiosulphate, it was necessary to seed the mixture in order to induce crystallisation.

In Fig. 1 the curve *ab* denotes solutions in equilibrium with solids along the line *a′b′*, which is so short that it gives only very slight evidence of mixed-crystal formation between $Na_2S_2O_3,5H_2O$ and (possibly) $Na_2SO_4,5H_2O$. The curve *bc* denotes solutions in equilibrium with solids along the line *b″c′*, and here there is definite evidence of mixed-crystal formation between decahydrates. The extent of this at 0·8° and 18° is approximately the same.

The two-phase dried solids along the line *b′b″*, which are in equilibrium with the solution at the condensed triple point *b*, were obtained by prolonged drying of the moist solid on blotting paper in a desiccator over the solution *b* at the temperature of the isotherm. Washing with alcohol resulted in partial dehydration of the crystals.

TABLE I.

Isotherm at 0·8°.

	Solutions.		Wet solids.		
Density.	% Na_2SO_4.	% $Na_2S_2O_3$.	% Na_2SO_4.	% $Na_2S_2O_3$.	Solid phases.
1·040	4·60	0·00	—	—	$Na_2SO_4,10H_2O$.
1·065	3·13	4·48	36·30	1·08	M.C. $Na_2SO_4,10H_2O$.
1·105	2·31	9·63	35·48	2·25	
1·159	1·88	16·03	31·91	4·95	
1·190	1·87	19·62	34·68	5·41	
1·247	1·56	25·63	32·14	8·38	
—	1·34	30·07	30·10	10·39	
1·312	1·27	32·26	32·84	9·28	
1·324	1·58	33·91	29·10	12·47	*
—	—	—	32·80	14·86	M.C. $Na_2SO_4,10H_2O$ and M.C. $Na_2S_2O_3,5H_2O$.
1·314	1·22	32·72	15·49	36·80	
—	—	—	15·83	39·67	
—	—	—	12·82	44·51	
1·317	1·15	32·77	9·10	45·07	
1·317	1·44	32·72	0·56	61·12	M.C. $Na_2S_2O_3,5H_2O$.
1·315	—	33·57	—	—	$Na_2S_2O_3,5H_2O$.

* Metastable.

TABLE II.

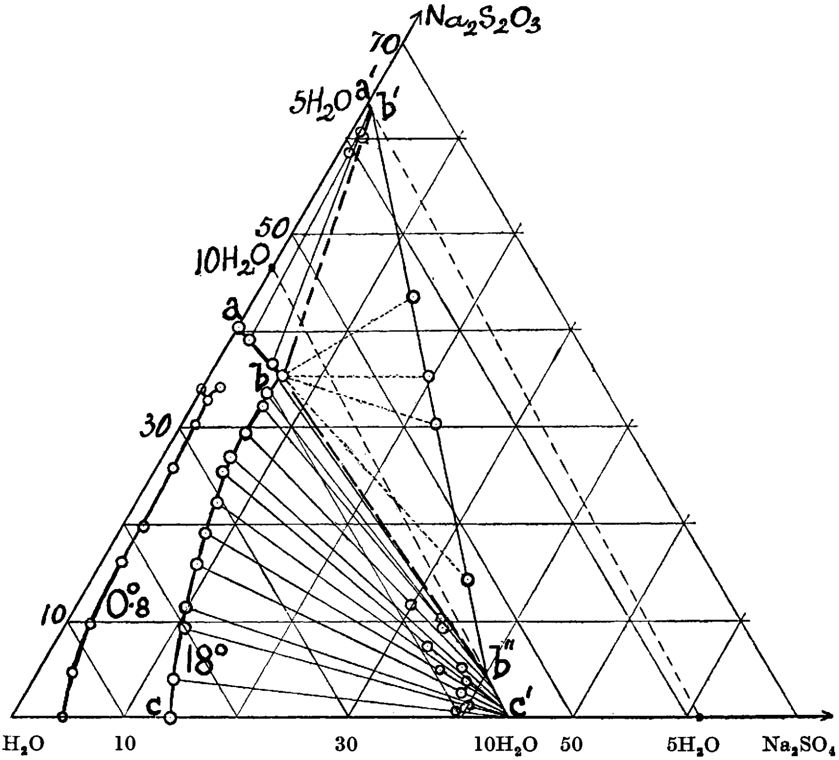
Isotherm at 18°.

	Solutions		Wet solids.		
Density.	% Na_2SO_4.	% $Na_2S_2O_3$.	% Na_2SO_4.	% $Na_2S_2O_3$.	Solid phases.
1·130	14·11	—	—	—	$Na_2SO_4,10H_2O$.
1·150	12·31	4·01	39·21	0·75	M.C. $Na_2SO_4,10H_2O$
1·180	10·71	9·36	40·14	1·21	
1·194	9·83	11·34	37·22	2·75	
1·225	8·45	15·86	38·75	2·52	
1·248	7·65	19·16	35·84	4·75	
1·276	7·14	22·46	38·64	3·60	
1·301	6·01	25·53	33·34	7·45	
1·314	5·97	27·00	37·59	5·11	
1·338	6·04	29·57	29·66	11·65	
1·356	6·32	32·31	33·92	9·18	
1·374	5·94	33·66	33·20	10·14	
1·390	6·14	35·07	34·12	9·63	
1·399	6·26	35·42	33·40	14·30	M.C. $Na_2SO_4,10H_2O$ and M.C. $Na_2S_2O_3,5H_2O$.
—	—	—	22·64	30·40	
—	—	—	19·40	35·46	
—	—	—	13·99	43·59	
1·394	6·31	35·46	1·02	60·02	M.C. $Na_2S_2O_3,5H_2O$.
1·395	4·87	36·61	0·79	60·73	
1·384	1·65	39·12	0·65	58·54	
1·378	—	40·36	—	—	$Na_2S_2O_3,5H_2O$.

The positions of these solids in the diagram along the line joining the end members, *b′* and *b″*, of the two series of mixed crystals provide strong evidence for the existence of the two series.

The isotherm at 40° (see Table III and Fig. 2) also consists of two curves, *ad* denoting solutions in equilibrium with solids along the line *a'd'*, and *df* solutions in equilibrium with solids along the line *d''f'*. Again the larger range is that of mixed crystals at the sulphate end, but at this temperature between anhydrous salts, whilst that showing mixed-crystal formation between $Na_2S_2O_3,5H_2O$ and (presumably) $Na_2SO_4,5H_2O$, although more extensive than at lower temperatures, is still very small. The dried solids along the line *d'd''* were obtained by washing the moist solid with warm methylated spirit and drying carefully between folded blotting paper. It was found very difficult in this case to remove all moisture from the solid owing to the finely-divided nature of the anhydrous sodium sulphate which was formed. The complexes in this isotherm were prepared by evaporation, under diminished

FIG. 1.



Isotherms at 0·8° *and* 18°.

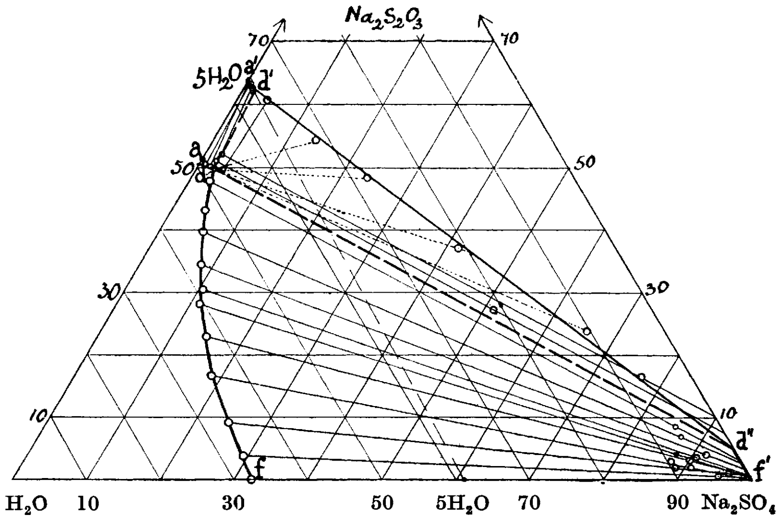
Table III.

Isotherm at 40°.

Solutions.			Wet solids.		
Density.	% Na_2SO_4.	% $Na_2S_2O_3$.	% Na_2SO_4.	% $Na_2S_2O_3$.	Solid phases.
—	32·37	—	—	—	Na_2SO_4.
—	29·35	3·79	95·25	0·37	M.C. Na_2SO_4.
1·326	24·79	9·06	96·23	0·84	
1·334	18·58	16·73	90·67	1·84	
—	14·76	22·95	90·50	2·87	
1·367	11·14	28·06	87·65	3·98	
—	10·40	30·44	90·85	3·29	
1·383	8·13	34·35	91·85	3·93	
—	5·90	39·74	86·98	6·80	
1·444	4·28	43·06	81·30	8·81	
1·484	2·46	48·78	85·56	8·29	
—	1·79	51·04	51·47	27·10	*
—	2·03	52·10	76·77	16·38	*
—	—	—	95·33	2·87	M.C. Na_2SO_4 and M.C. $Na_2S_2O_3,5H_2O$.
1·496	2·27	49·38	65·72	23·80	
1·496	2·08	49·72	41·80	37·03	
1·494	2·24	49·73	23·68	48·26	
—	2·09	49·97	13·82	54·14	
—	3·61	49·60	4·06	60·68	* M.C. $Na_2S_2O_3,5H_2O$.
1·493	2·14	49·88	1·51	62·00	
—	2·45	49·98	0·28	63·41	
—	1·58	50·15	0·00	63·26	
1·492	0·67	50·49	0·00	64·58	
1·488	—	51·23	—	—	$Na_2S_2O_3,5H_2O$.

* Metastable.

Fig. 2.

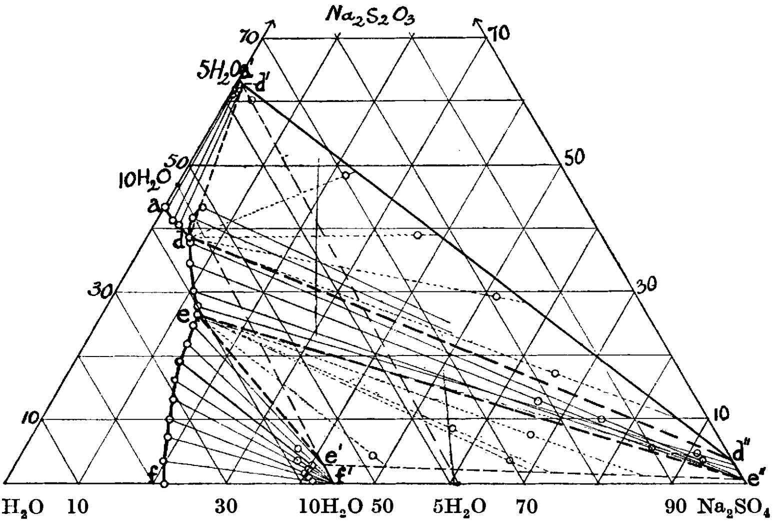


Isotherm at 40°.

pressure, of solutions unsaturated at 40°, using the method employed by Rivett and Lewis (J., 1924, **125**, 1163).

The transition point between decahydrated and anhydrous sodium sulphate will be depressed by the addition of sodium thiosulphate to the solution. With an appropriate mixture in a Dewar flask fitted with thermometer and stirrer, temperature–time curves on heating and cooling were obtained. The mixture was heated at 70° for an hour to hasten the formation of mixed crystals and then cooled to 15°, being well inoculated with crystals of $Na_2S_2O_3,5H_2O$ and $Na_2SO_4,10H_2O$. On slow re-heating, this gave a well-defined arrest at 20·30° and on cooling at 19·80°. These temperatures were accurately reproducible, both with the same and with fresh mixtures. The cooling curve was of the usual form, showing undercooling followed by a rise in temperature to the arrest point on seeding. Samples of the solutions in equilibrium with the three solid phases at the arrest points, both on heating and on cooling, were drawn off and analysed, the mean composition being 7·95% of sodium sulphate and 35·0% of thiosulphate. The difference between the two temperatures is probably accounted for by the slow rate of diffusion in the solid phases, the mixed crystals forming above and below the quadruple point being of slightly different compositions. The true transition point should lie between these two temperatures, at about 20·05°.

Fig. 3.



Isotherm at 25°.

TABLE IV.

Isotherm at 25°.

Solutions.			Wet solids.		
Density.	% Na_2SO_4.	% $Na_2S_2O_3$.	% Na_2SO_4.	% $Na_2S_2O_3$.	Solid phases.
1·204	21·60	—	—	—	$Na_2SO_4,10H_2O$.
1·215	19·74	3·48	41·43	0·34	M.C. $Na_2SO_4,10H_2O$.
1·236	18·44	7·30	40·39	1·06	
1·253	17·12	10·14	39·79	1·56	
1·271	16·13	13·22	39·88	2·23	
1·288	14·86	16·16	37·80	3·50	
1·311	13·97	19·35	40·07	2·94	
—	13·62	22·02	36·85	5·51	
1·359	12·97	24·96	—	—	
—	—	—	47·50	4·44	M.C. $Na_2SO_4,10H_2O$, and M.C. Na_2SO_4.
—	—	—	66·38	3·60	
—	12·72	26·86	56·17	8·65	
—	12·72	26·65	67·08	7·77	
—	13·27	26·12	92·50	3·53	* M.C. Na_2SO_4.
1·379	12·15	28·00	91·15	4·70	
—	10·28	30·31	84·66	5·52	
1·401	7·73	34·72	65·45	12·94	
—	6·06	38·07	75·62	10·08	
—	4·53	41·86	—	—	*
1·453	4·87	43·32	—	—	*
—	5·59	38·83	65·72	17·16	M.C. Na_2SO_4 and M.C. $Na_2S_2O_3,5H_2O$.
—	5·66	38·67	51·92	29·11	
1·426	5·64	38·97	36·12	38·99	
1·420	5·42	38·85	21·86	48·30	
—	5·20	38·96	3·36	60·33	
1·418	4·69	39·45	0·92	61·97	M.C. $Na_2S_2O_3,5H_2O$.
1·412	3·13	40·92	0·00	63·46	
1·411	2·01	41·53	0·51	61·14	
1·410	0·23	43·52	0·22	62·32	
—	—	43·50	(from tables)		$Na_2S_2O_3,5H_2O$.

* Metastable.

The isotherm at 25° should then show three curves, since three solid phases may exist at this temperature. The results obtained are in Table IV and are plotted in Fig. 3. The isotherm consists of three curves: *ad* denoting solutions in equilibrium with mixed crystals along the small range *a'd'* (mainly $Na_2S_2O_3,5H_2O$), *de* denoting those in equilibrium with mixed crystals along the line *d''e''* (mainly anhydrous Na_2SO_4), and *ef*, where the equilibrium is with mixed crystals along *e'f'* (mainly $Na_2SO_4,10H_2O$). The solids along *e''e'* were dried on blotting paper and those along *d'd''* were washed with spirit.

The existence of mixed crystals of decahydrates of the two salts and of a very small range of pentahydrates is clearly shown. The evidence obtained here for the series of mixed crystals of anhydrous salts is not definite, but the work at 40° points to the existence of an analogous series at 25°. The solutions in this isotherm were prepared by dissolving the salt constituent which should mainly constitute the solid phase in the total amount of water required, then adding the other salt, and rotating the tube in the bath.

The sodium sulphate solution curve has been extended into the metastable region at 0·8°, 25° and 40°, and in each case it shows a decided increase in curvature. If the metastable solution curve in a system where mixed crystals are formed could be fully realised, it should form a closed loop, and this is indicated by the shapes of the curves in the metastable region.

Summary.

1. The system sodium thiosulphate–sulphate–water has been examined at 0·8°, 18°, 25°, and 40°.

2. The existence has been demonstrated of a very short series of mixed crystals of pentahydrates at all four temperatures; of a series of decahydrates at 0·8°, 18°, and 25°; and of a series of anhydrous salts at 25° and 40°.

3. The quadruple point at which four phases co-exist, three being mixed crystals and one a solution, is at a temperature very close to 20°.

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UNIVERSITY OF MELBOURNE.

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