

296. *The Ternary System : Stannous Oxide–Sulphur Trioxide–Water.*

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THE well-known amphoteric nature of stannous oxide is closely associated with the tendency of the stannous salts to undergo extensive hydrolysis in aqueous solution, resulting generally in the precipitation of basic salts. Although numerous such basic sulphates have been described, there appears to have been no systematic phase-rule study of the problem; indeed, the methods applied by many workers were almost certain to have led to precipitation of variable mixtures of basic salts. This paper describes a systematic study of the above system at 25° and 50° in order to fix the identity of the basic sulphates capable of existence in stable equilibrium with the solutions chosen. Schreinemakers's system of plotting results has been employed, the composition of the solid phases being found by the "residue" method (*Z. physikal. Chem.*, 1893, **11**, 76).

In all cases the complexes were made from hydrated stannous oxide, sulphuric acid, and the amount of water calculated to give the desired proportion. When the composition of the complexes lay on the acid side, it was readily possible to obtain equilibrium by shaking together for 3 days the necessary quantities of the oxide, acid, and water, but on the basic side difficulty was experienced, even after some weeks' shaking, almost certainly owing to the separation of more than one basic salt resulting from the manner in which the mixing had been done. It was found more suitable to bring together the stannous oxide and sulphuric acid, and after these had reacted, the required amount of water was added with stirring.

The stannous oxide was made by running a saturated solution of the sulphate, previously treated with granulated tin, into 2*N*-ammonia. This oxide, after being rapidly washed and dried in a vacuum, contained SO₃, 0.6; H₂O, 21.4%, due allowance for the presence of these components being made when the complexes were prepared. Water used for the preparation of the complexes and for the washing of the precipitated stannous oxide was freed from air by boiling, and then cooled in a stream of nitrogen. The flasks containing the complexes were filled with nitrogen prior to being sealed off. No definite indication of the presence of stannic oxide in the stannous oxide could be obtained.

In all the determinations of sulphate, owing to the tendency of barium sulphate to carry out with it varying amounts of tin compounds, it was found advisable to add barium chloride to a boiling solution of the tin compound containing 20 c.c. of concentrated hydrochloric acid per 200 c.c. of water. This method gave accurate results when checked against a solution containing potassium sulphate and the same solution to which various amounts of stannous chloride had been added.

The analytical results shown in the tables are plotted in Figs. 1 and 2. Reference to these graphs shows the very restricted area in which the tetrahydrate SnSO₄·2SnO·4H₂O is capable of existence in contact with its saturated solution at 25°, and the even more restricted area at 50° wherein the dihydrate SnSO₄·2SnO·2H₂O exists. It was therefore deemed advisable to confirm the location of the point of intersection of the tie-lines by preparing samples of these solids by the "porous plate" method. The drying of the solids was carried out under equilibrium conditions, the solid spread out on a porous plate being confined in a desiccator for some weeks at the temperature of the isotherm under review in contact with the vapour of its equilibrium solution. The solids were then analysed, with the following results:

Dry solid A at 25°: SnO, 72.8; SO₃, 14.2; H₂O, 13.0. Calc. for SnSO₄·2SnO·4H₂O: SnO, 72.67; SO₃, 14.39; H₂O, 12.94%.

Dry solid A at 50°: SnO, 78.5; SO₃, 14.5; H₂O, 7.0. Calc. for SnSO₄·2SnO·2H₂O: SnO, 78.06; SO₃, 14.67; H₂O, 7.27%.

FIG. 1.

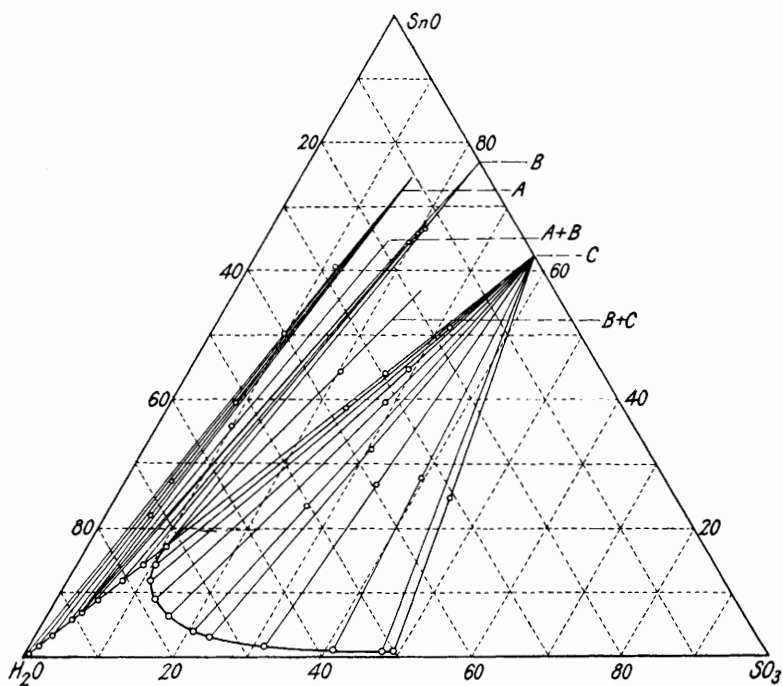
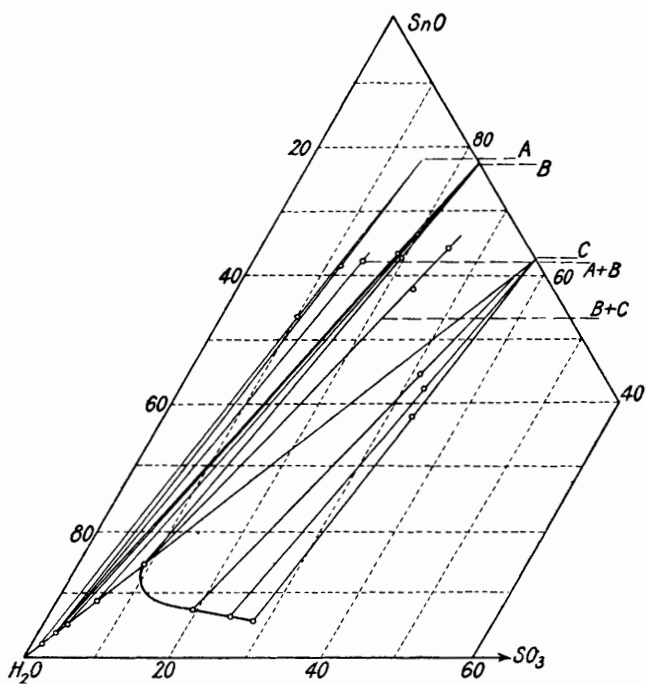


FIG. 2.



D.	Solution.			Wet solid.			Solid phase.
	SnO.	SO ₃ .	H ₂ O.	SnO.	SO ₃ .	H ₂ O.	
1·004	0·30	0·20	99·50	61·1	11·8	27·1	A
1·030	2·21	1·36	96·43	50·8	9·94	39·26	A
1·040	3·07	1·87	95·06	27·66	6·06	66·34	A
1·053	3·70	2·20	94·10	46·53	9·70	43·77	A
1·065	4·56	2·76	92·68	39·90	8·26	51·84	A
1·080	5·72	3·39	90·89	22·61	6·00	71·39	A
1·090	6·30	3·72	89·98	36·00	10·10	53·90	A, B
1·120	8·02	4·85	87·13	66·80	19·80	13·40	B
1·150	9·68	5·77	84·55	69·10	20·84	10·06	B
1·185	11·68	6·79	81·53	66·10	19·46	14·44	B
1·188	11·90	6·90	81·20	65·66	19·20	15·14	B
1·250	15·15	8·87	75·98	68·70	20·83	10·47	B
1·270	16·30	9·50	74·20	44·40	15·15	40·45	B
1·270	16·26	9·53	74·21	69·40	21·02	9·58	B
1·300	17·50	10·27	72·23	44·30	24·40	31·30	B, C
1·265	14·64	10·52	74·84	45·10	24·20	30·70	C
1·250	12·78	10·44	76·78	51·36	30·92	17·72	C
1·240	11·83	10·64	77·53	48·70	29·84	21·46	C
1·220	9·43	12·85	77·72	45·30	29·20	25·50	C
1·210	6·39	15·92	77·69	39·80	28·50	31·70	C
1·223	3·80	20·35	75·85	33·34	28·80	37·86	C
1·239	2·98	23·00	74·02	36·55	30·80	32·65	C
1·307	1·50	31·30	67·20	33·50	34·50	32·00	C
1·404	0·60	40·90	58·50	34·25	39·00	26·75	C
1·508	0·36	49·63	50·01	29·34	44·00	26·66	C

A = SnSO₄·2SnO·4H₂O; B = SnSO₄·SnO; C = SnSO₄.

Results at 50°.							
1·018	1·04	0·68	98·28	53·10	10·10	36·80	A
1·037	2·53	1·53	95·94	61·50	15·70	22·80	A, B
1·058	3·80	2·17	94·03	64·20	18·54	17·26	B
1·145	9·33	5·64	85·03	67·33	19·82	12·85	B
1·230	14·00	8·30	77·70	63·36	19·30	17·34	B
1·244	14·80	8·70	76·50	65·70	22·61	11·69	B, C
1·246	14·82	8·78	76·40	59·30	20·00	20·70	B, C
1·220	8·74	14·12	77·14	44·10	29·42	26·48	C
1·263	7·42	19·66	72·92	42·65	30·94	26·41	C
1·326	5·06	28·43	66·51	38·60	33·80	27·60	C

A = SnSO₄·2SnO·2H₂O; B = SnSO₄·SnO; C = SnSO₄.

The non-existence of the dihydrated stannous dioxysulphate at 25° indicates that at some definite temperature between 25° and 50° a second invariant point appears at the transition point between the tetrahydrated stannous dioxysulphate and the anhydrous monoxysulphate, giving rise to a new area representing a solid phase of composition SnSO₄·2SnO·2H₂O in equilibrium with a solution of varying composition. This new area grows with rising temperature at the expense of the area representing the tetrahydrate and its equilibrium solutions until finally this hydrate is eliminated altogether at some temperature below 50°.

SUMMARY.

The existence has been established at 25° of stannous dioxysulphate tetrahydrate, and at 50° of the dihydrate (cf. Ditte's SnSO₄·2SnO₂·1·5H₂O, *J.*, 1883, **44**, 294; and Carson's SnSO₄·2·017—2·098SnO₂·xH₂O, *J. Amer. Chem. Soc.*, 1926, **48**, 906), and also of an anhydrous stannous monoxysulphate, stable at both temperatures, in agreement with Carson's isolation of this salt.

The solubility of stannous sulphate in sulphuric acid at 25° and 50° has been determined, the results giving no evidence of a hydrated normal sulphate.

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