CCLXXXI.—*The Systems* B_2O_3–SO_3–H_2O *and* B_2O_3–P_2O_5–H_2O.

By MIRIAM LEVI and LIONEL FELIX GILBERT.

(i) *The System* B_2O_3–SO_3–H_2O.

MERZ (*J. pr. Chem.*, 1866, **99**, 81) stated that when equal weights of boric and concentrated sulphuric acids were heated to constant weight at 250—280° a substance was obtained of composition $5B_2O_3,2SO_3,2H_2O$. Gmelin reported (*Ann. Supp.*, 1867, **5**, 165) that boron trioxide and boric acid dissolved extensively in concentrated sulphuric acid on heating, and that on cooling a thick syrup was obtained which deposited hydrates of boric acid on standing in moist air. Schultz-Sellack (*Ber.*, 1871, **4**, 12) found that the solution of boric acid in concentrated sulphuric acid gave on evaporation a viscous or glassy mass, which was not of constant composition. If, however, the sulphuric acid solution was treated with sulphur trioxide, or if boron trioxide was added to fuming sulphuric acid, leafy crystals, of composition $B_2O_3,3SO_3,H_2O$, were obtained on evaporation.

D'Arcy (J., 1889, **55**, 155) could not confirm the existence of Merz's or Schultz-Sellack's compounds. He reports that on mixing boric acid with excess of sulphur trioxide a violent reaction occurs; on heating the mixture at 100° till no more fumes are evolved and then cooling, a white substance separates of composition $B_2O_3,6SO_3,3H_2O$. Herz (*Z. anorg. Chem.*, 1903, **34**, 205) has made solubility measurements of boric acid in four different concentrations of sulphuric acid, $9N$ being the highest; no examination of the solid phases was made.

In the present work, a partial survey of the condensed ternary system has been made at 25° and 45° by the Schreinemakers method, supplemented by direct analyses of the solid phases. None of the above compounds has been found to exist under our experimental conditions, but the new compounds $B_2O_3,SO_3,4H_2O$ and $3B_2O_3,SO_3,3H_2O$ appear to be definitely characterised.

The reactants supplying the components were, in addition to water, concentrated sulphuric acid, fuming sulphuric acid, boric acid, and a specimen of powdered boron trioxide containing about 13% of water. These substances were in each case of a satisfactory degree of purity.

The boric–sulphuric acid mixtures examined were analysed by Herz's method (*Z. anorg. Chem.*, 1903, **33**, 353), which was tested and found to be very accurate, although the few solubilities recorded by that author do not agree with ours (see below), possibly owing to the fact that in determining them he used a less accurate method (compare Kendall and Andrews, *J. Amer. Chem. Soc.*, 1921, **43**, 1550). The procedure was to titrate suitably diluted solutions with $0{\cdot}1N$-sodium hydroxide in the presence of *p*-nitrophenol as indicator until the first yellow colour appeared, corresponding with the neutralisation of the sulphuric acid; 10 c.c. of a neutral, saturated solution of mannite and two drops of phenolphthalein solution were then added, and the titration was continued until a definite pink colour persisted for 3 minutes. This latter amount of alkali was equivalent to the boric acid present.

The solubility determinations were complicated, when high concentrations of sulphuric acid were concerned, by the ease with which highly supersaturated solutions were obtained, even when solution was effected at room temperatures. This tendency was especially marked in the region relating to the solid phase, $B_2O_3,SO_3,4H_2O$.

In some cases, solutions stood for several weeks before any solid phase commenced to separate, and the further precipitation was also very slow. None of the usual methods for overcoming this type of difficulty, *viz.*, cooling, heating, or the addition of foreign bodies or of the appropriate solid phase, seemed to have any marked effect.

Three methods of obtaining the necessary data for the ternary diagram were employed.

(*a*) The well-known method of agitating in a thermostat sealed glass tubes containing the reactants mixed in suitable proportions was employed for low concentrations of sulphuric acid, where equilibrium was easily attained. As soon as a tube was opened, the liquid and the wet solid were rapidly sampled and the samples were transferred to a specific-gravity bottle in the thermostat and to a weighing bottle, respectively.

(*b*) The reactants were stirred with dry air in an apparatus similar to that used by Donnan and White (J., 1911, **99**, 1788), the Gooch crucible used by these authors for separating solid and liquid being here replaced by a glass filter-funnel with a permanently fixed filter-plate of fritted glass. This method was used with some of the higher concentrations of (non-fuming) sulphuric acid, where the attainment of equilibrium was too slow by the tube method.

(*c*) The reactants were placed in a glass bottle of about 500 c.c. capacity, fitted with a glass stirrer passing through a mercury seal. After long stirring, the solid was allowed to segregate and samples of liquid and solid were taken. This method was used for mixtures containing fuming sulphuric acid, and for some other mixtures of high viscosity.

Compositions of saturated solutions and of their respective wet solids are shown in Table I and Fig. 1 for 25°, and in Table II for 45°. Although Herz's solubilities were determined at 26°, they are consistently lower than our values for 25°; *e.g.*, the concentration of boric acid in $8{\cdot}75N$-sulphuric acid is $0{\cdot}092N$ (Herz) and about $0{\cdot}37N$ by interpolation from our results. Areas corresponding to three distinct solid phases will be observed in Fig. 1, *viz.*, $B_2O_3,3H_2O$ (*i.e.*, H_3BO_3), $B_2O_3,SO_3,4H_2O$, and $3B_2O_3,SO_3,3H_2O$, but there is no evidence here for any of the ternary compounds described by other authors. On plotting the 45°-data, a similar

TABLE I.

	Solutions. Composition (g./100 g.).		Wet solids. Composition (g./100 g.).		
$d^{25°}_{4°}$.	SO_3.	B_2O_3.	SO_3.	B_2O_3.	Solid phase.
1·017	0·00	3·08*			H_3BO_3.
1·032	1·96	2·87	0·70	35·76	
1·039	2·90	2·79			
1·088	9·12	2·18	4·82	28·82	
1·112	11·85	2·00			
1·160	17·56	1·54			
1·270	28·82	1·04			
1·284	30·62	0·97	19·90	20·26	
1·305	32·78	0·87	18·94	24·78	
1·412	41·78	0·71	30·33	15·98	
1·446	44·44	0·68	27·74	21·60	
1·479	46·80	0·65	26·68	24·84	
	53·94	1·46	3·89	52·19	
	54·89	1·47			
1·625	55·84	2·69	47·22	10·79	
	54·66	6·09			
	54·16	7·17	35·30	23·98	
1·668	53·50	8·12	37·80	22·30	
	55·74	7·70	45·03	20·01	$B_2O_3,SO_3,4H_2O$.
1·617	54·73	10·32	48·19	17·76	
	54·20	11·73			
	51·87	15·45	49·34	18·02	
	47·27	20·93			
	51·87	21·85			$3B_2O_3,SO_3,3H_2O$.
	52·89	21·06	38·72	40·64	
	57·32	18·34	41·47	38·54	
	61·44	16·07	43·71	37·34	
	63·36	15·23			
	70·02	12·00	52·61	30·05	
1·882	73·66	10·39	59·50	24·90	
	86·24	5·07			
	86·50	4·96			
	87·72	4·82	43·43	43·45	

* In agreement with Kendall and Andrews (*loc. cit.*).

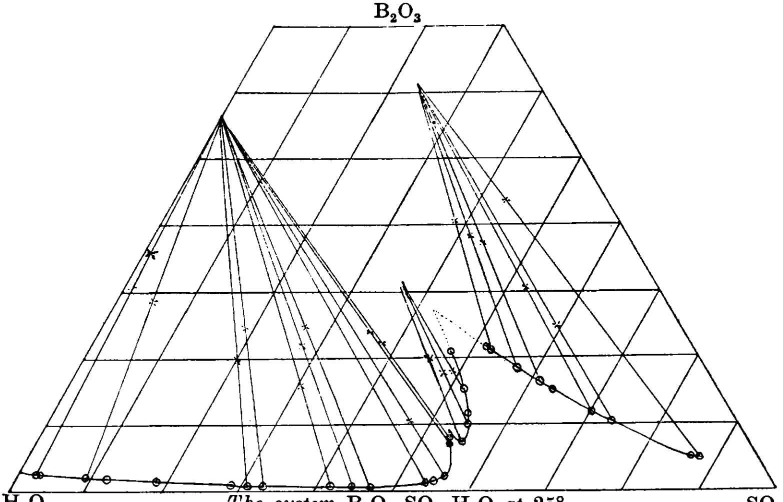
TABLE II.

	Solutions. Composition (g./100 g.).		Wet solids. Composition (g./100 g.).		
$d^{45°}_{4°}$.	SO_3.	B_2O_3.	SO_3.	B_2O_3.	Solid phase.
1·023	0·00	5·17			H_3BO_3.
1·029	0·47	5·07	0·13	38·37	
1·036	1·93	4·83	0·71	34·57	
1·086	8·58	3·74	4·86	28·88	
1·097	10·18	3·51	5·78	26·54	
1·231	25·48	1·89	15·48	23·33	
1·446	44·87	0·13	33·73	13·98	
1·628	52·25	7·07	37·81	20·52	
1·671	54·13	8·33	45·45	19·83	$B_2O_3,SO_3,4H_2O$.
1·685	56·65	6·14	49·50	15·21	
	60·89	4·89	49·49	17·89	
	62·66	6·85	47·35	21·05	
1·800	57·22	13·56			
	59·87	23·60	41·08	35·18	$3B_2O_3,SO_3,3H_2O$.
	57·70	19·25	41·34	40·29	
	60·43	17·99	46·64	35·66	

solubility curve to that at 25° is obtained, but the tie-lines corresponding to the two new compounds are not so satisfactorily convergent. The attainment of equilibrium was too slow for more satisfactory data to be obtained, but it is considered that there is little doubt that the above compounds are also obtained at 45°. The quite characteristic appearances of the solid phases were also similar to those obtained at 25°.

Samples of the two new solids, prepared by the interaction of boric acid with 88% sulphuric acid, and of boron trioxide (87%) with concentrated sulphuric acid, respectively, and kept in desiccators on carefully dried porous plates, gave the following analyses:

FIG. 1.



The system B_2O_3–SO_3–H_2O *at* 25°.

	$B_2O_3,SO_3,4H_2O$.				$3B_2O_3,SO_3,3H_2O$.			
	I.	II.	III.	Calc.	I.	II.	III.	Calc.
% SO_3	36·6	36·1	36·6	36·0	22·1	25·4	24·9	23·3
% B_2O_3	31·2	32·3	32·0	31·5	64·8	61·9	59·5	61·0

It is considered that discrepancies between observed and calculated results can fairly be ascribed to a certain amount of hydrolysis which may have occurred on sampling, and also to the difficulty of draining the viscous adherent liquids, the viscosity of which is especially high in the case of the second compound.

$B_2O_3,SO_3,4H_2O$ is a white, finely-divided, crystalline substance; $3B_2O_3,SO_3,3H_2O$ consists of larger, colourless crystals. Both compounds rapidly absorb moisture from the atmosphere, with consequent decomposition.

Viscosities of Solutions of Boric Acid in Concentrated Sulphuric Acid.—A few determinations were made at 25° of the viscosities of solutions of boric acid in concentrated sulphuric acid compared with that of the solvent, by the capillary flow method. No great accuracy is claimed for these measurements, which, however, help to emphasise some of the difficulties experienced when working with this system. The results obtained were :

% H_3BO_3	0	8·5	15·9	24·5	30·0	37·6	42·7
Relative time of flow	1	3·96	12·5	40·1	84·0	219	440

(ii) *The System* B_2O_3–P_2O_5–H_2O.

Vogel (*Z. anal. Chem.*, 1870, **9**, 376) obtained a compound containing " an equal number of equivalents of boric and phosphoric acids " by strongly heating mixtures of these substances. Meyer (*Ber.*, 1889, **22**, 2919), Mylius and Meusser (*Ber.*, 1904, **37**, 397), and Prescher (*Arch. Pharm.*, 1904, **242**, 199) all obtained a substance of empirical composition BPO_4 by methods similar to that of Vogel, whose compound, therefore, was probably the same (compare Comey, " Dictionary of Chemical Solubilities," 1921, p. 668). BPO_4, thus prepared, is insoluble in water and only slowly decomposed by boiling alkalis. Mylius and Meusser observed, however, that, when formed at comparatively low temperatures (80—100°) from the above reactants, or from solutions of metaboric acid in acetic and phosphoric acids or from solutions of boric acid in phosphoric and concentrated sulphuric acids, BPO_4 is soluble in water with decomposition, but becomes insoluble on heating to 400°. Gustavson (*Ber.*, 1871, **4**, 975) made BPO_4 by heating boron trioxide with phosphorus pentachloride, and boron trichloride with phosphorus pentoxide. Apparently here, too, the soluble compound was first formed and became insoluble on further heating.

The ternary system B_2O_3–P_2O_5–H_2O at 25° has now been partially investigated, and BPO_4 occurred as the solid phase in one of the regions under examination.

Well-boiled syrupy phosphoric acid, free from phosphorous acid, was employed as the source of phosphorus pentoxide, and was suitably diluted as required. The boric acid and boron trioxide used were similar specimens to those mentioned previously.

On examination of the literature, Kolthoff's method (*Chem. Weekblad*, 1922, **19**, 449) appeared to be the most suitable for the rather difficult determination of mixtures of boric and phosphoric acids, but it was found not to give sufficiently accurate results. In addition to the difficulty of distinguishing between various shades of pink, it was found that the titration value for the phosphoric acid end-point varied with the amount of boric acid present if the titration was carried on until the same p_H value was obtained in each case. Whilst retaining the use of sodium citrate and Kolthoff's p_H value for the total-acid end-point, which was found to be correct and unaffected by the relative amounts of the acids, a new procedure was adopted. 0·1*N*-Mixtures of known composition of boric and phosphoric acids were made up, 10 c.c. of 40% sodium citrate solution and thymol-blue were then added, followed by the appropriate amount of 0·1*N*-sodium hydroxide to convert all the phosphoric acid to the secondary sodium salt. The p_H numbers acquired by the solutions were then determined by comparison with a colour chart, and plotted against the % of boric acid molecules in the total acid molecules present.

The correction graph was plotted from the following data, of which the accuracy is considered sufficient for the purpose :

% H_3BO_3......	100	96	82	70·5	58	52	40·5	35	26·3	15·5	0
p_H	8·2	8·3	8·4	8·5	8·6	8·7	8·8	8·9	9·0	9·1	9·2

In the analysis of an unknown mixture the % of boric acid was first determined roughly and the corresponding p_H number read off the graph. Exact determinations were then made on 25 c.c. of another sample by titrating with caustic soda (in presence of sodium citrate and thymol blue) to this p_H number, thus allowing the amount of phosphoric acid to be calculated; 10 c.c. of a saturated solution of mannite were then added and the solution was titrated until the colour corresponding to p_H 8·7 lasted for at least a minute. This latter volume of sodium hydroxide was equivalent to the boric acid present. A test of the method over a wide range of relative concentrations of the acids indicated that it gave very accurate results.

The first two methods employed in the preceding system were found suitable for obtaining the solubility and wet-solid data. Some difficulty was experienced in filtering satisfactorily mixtures made with high concentrations of phosphoric acid. Large quantities of boric acid and boron trioxide will dissolve in such phosphoric acid solutions with the formation of clear liquids from which a new, very finely divided, solid phase slowly separates. This coagulates slightly and settles after 3 or 4 days, but still passes through filters of average pore diameter 35—40 × 10^{-4} and in some cases even 4—5 × 10^{-4} cm.

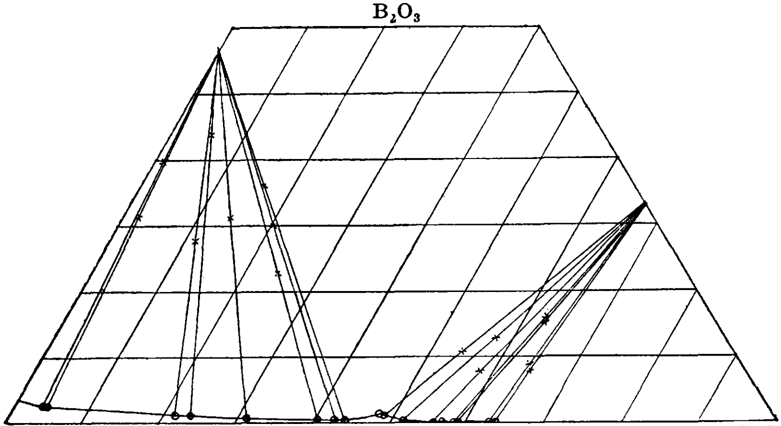
The results obtained are shown in Table III and partly in Fig. 2. The solid phase in equilibrium with solutions containing up to about 48% of P_2O_5 is boric acid, after which BPO_4 or some polymeride is formed. The BPO_4 thus obtained is the water-soluble variety. Attempts to prepare a pure dry specimen have so far

TABLE III.

	Solutions.		Wet solids.		
	Composition (g./100 g.).		Composition (g./100 g.).		Solid
$d_{4^\circ}^{25^\circ}$.	P_2O_5.	B_2O_3.	P_2O_5.	B_2O_3.	phase.
1·042	3·63	2·55	1·23	39·80	H_3BO_3.
1·048	4·34	2·53	2·04	31·35	
1·190	21·51	1·12	11·09	27·91	
1·215	23·66	1·05	5·39	43·86	
1·281	31·01	0·62	14·10	31·03	
1·391	40·39	0·45	24·28	22·89	
	42·60	0·68	20·13	30·03	
1·434	43·70	0·68	16·11	35·78	
1·504	48·08	1·27	45·62	13·59*	
1·516	48·51	1·20			BPO_4.
	48·89	1·11	54·43	10·49	
	51·52	0·23	57·81	12·70	
	55·37	Concentration too low to be titrated.	58·12	7·50	
	56·99				
	58·35		62·73	15·9	
1·645	58·68		62·81	15·02	
	62·81		64·06	8·95	
1·722	63·43		64·40	7·94	

* Apparently point of inversion.

FIG. 2.



The system B_2O_3–P_2O_5–H_2O *at* 25°.

been unsuccessful. BPO_4 retains the viscous supernatant liquid very strongly and is rapidly attacked by atmospheric moisture. It appears to be a white, finely-divided powder.

THE WILLIAM RAMSAY INORGANIC AND
PHYSICAL CHEMISTRY LABORATORIES,
UNIVERSITY COLLEGE, LONDON.

[*Received, June* 7*th*, 1927.]