

LXXVIII.—*The Boric Acids.*

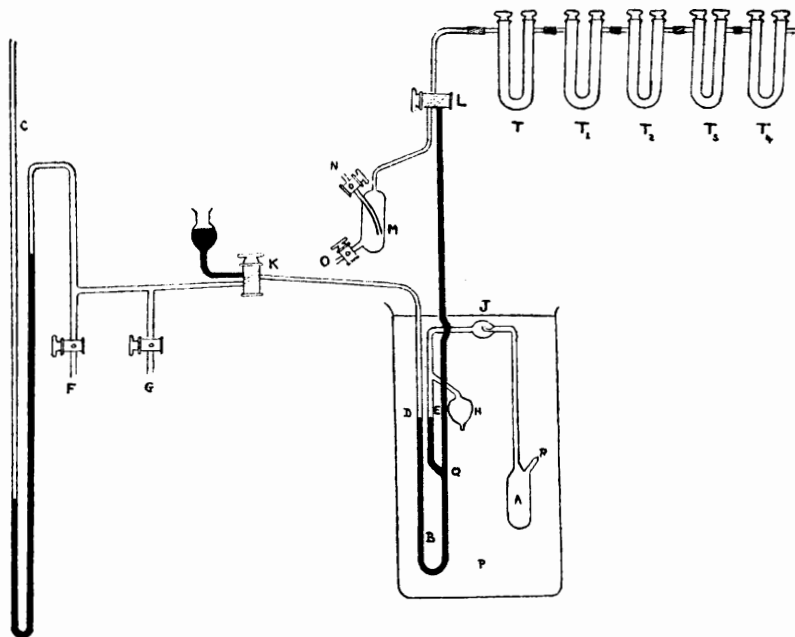
By LIONEL FELIX GILBERT and MIRIAM LEVI.

SEVERAL compounds of boric anhydride with water in various proportions have been reported, but examination of the original literature shows that in many cases the experimental evidence for their existence is inadequate. When the work now described was commenced, the following statement by Little (Friend's "Text-book of Inorganic Chemistry," Vol. IV) seemed to be well justified: "At the present time, the existence in the solid state of only two of the boric acids, orthoboric acid, H_3BO_3 (*i.e.*, $B_2O_3 \cdot 3H_2O$), and metaboric acid, HBO_2 (*i.e.*, $B_2O_3 \cdot H_2O$), can be definitely affirmed."

It was decided to attempt to solve the problem by a method similar to that commonly employed in investigating a series of salt hydrates, *viz.*, by combining determinations of vapour pressures in the system $B_2O_3-H_2O$ with measurements of weights of water lost in passing from one part of the system to another.

After a number of trials, an apparatus of the type shown in Fig. 1 (which is not to scale) was evolved. Considered from the point of view of pressure measurements it is similar to that employed by Caven and Sand (J., 1911, **99**, 1359), but differs in that it has provision for the withdrawal and quantitative collection of water vapour. The apparatus thus modified is very suitable for the examination of many types of equilibria such as those described here.

FIG. 1.



The bulb, A, containing the mixture under examination is connected through the mercury gauge, B, maintained at the same temperature, to the manometer, C; when the levels of the mercury in the limbs, D and E, of the mercury gauge are the same, the pressure in A can be read directly at C. The taps, F and G, are connected respectively to a pump and to the atmosphere *via* a drying tube, so the pressure in the apparatus, and consequently the levels in D and E, can be adjusted as required. H is a bulb which is of use when the pressure in A decreases during experiments, preventing mercury from running back into A. A further safety trap, J, is provided. Mercury can be introduced at the three-way tap, K. The special form of the mercury gauge allows water vapour to be removed at the tap L, which is connected through a mercury

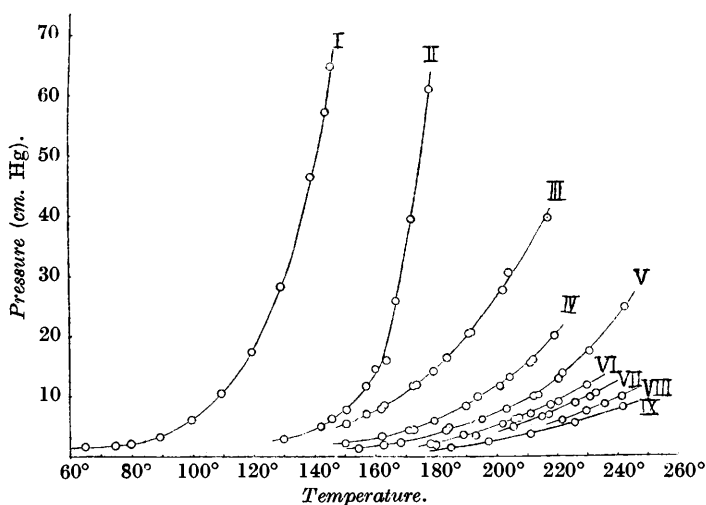
trap, T, to a series of weighed drying tubes, T₁, T₂, etc., the first containing calcium chloride and the remainder phosphoric oxide. The last drying tube is connected through a guard tube to a Hyvac pump. It was found possible to dispense with some of the drying tubes in the later stages of the experiments, where little water was evolved. L can be put into communication also with a trap, M, connected at N to calcium chloride towers; this enables a stream of dry air to be drawn through the apparatus above L, thus accelerating the transfer of water to the drying tubes. A tap, O, is provided for withdrawing mercury, which from time to time falls into M when it is connected to the drying tubes.

Heating was effected by means of electrically heated B.P. paraffin in a 5-litre beaker, P, stirred by an electrically driven paddle placed in the centre. A modified form of thermo-regulator described by Lewis and Wood (*Trans. Faraday Soc.*, 1921, **17**, 696) was used. Temperature was measured by a glass-mercury thermometer with the bulb close to A. The bath liquid was not entirely satisfactory, for at temperatures above 100° it darkened rapidly, eventually becoming so black that it was impossible to continue reading the mercury gauge. Fresh oil had therefore to be substituted from time to time.

The experimental procedure was as follows. A known weight of powdered boric acid was placed in A, through the side-tube, R, which was then sealed off, after which the apparatus was evacuated at room temperature through the tap F. Mercury was then run in at K until the side-tube at Q was sealed, the levels in D and E being the same. The bath was then heated to a suitable temperature, the water vapour evolved exerting a pressure which eventually depressed the mercury in E to Q, thus allowing the vapour to pass up the tube QL. A small quantity of vapour (which was afterwards collected in the drying tubes) was withdrawn from A in this way in order to help to remove any adsorbed atmospheric gas still remaining which had not been removed during the initial evacuation at the lower temperature. When sufficient vapour had been withdrawn, the mercury was raised above Q by suitable manipulation of the taps F and G, and the levels D and E were kept approximately equal until equilibrium resulted. A careful adjustment of the levels was then made, and the pressure was read at C. To ensure that equilibrium had been attained, the pressure was allowed to remain constant for at least $\frac{1}{2}$ hour before the decisive reading was taken. (This period sufficed for the higher hydrates, but not for the lower hydrates, where the attainment of equilibrium was much slower.) In many cases, further to ensure that equilibrium had been attained, the temperature of the bath was raised by 1–2° and then allowed to

revert to the temperature under consideration. The temperature was then raised by 10° steps, approximately, a series of points upon curve I in Fig. 2 thus being obtained, after correction for the vapour pressure of mercury, for which Ramsay and Young's values (J., 1886, 49, 37) were used. The temperature range was then similarly traversed in the reverse direction. Equilibrium was thus approached from both high and low temperatures. To proceed to the next hydrate system, a suitable temperature was selected, and equilibrium allowed to take place. The pressure in E was then lowered so that vapour from A could escape through Q and rise up through the mercury in the tube QL. Much of the water condensed at the top

FIG. 2.



of the tube, which was relatively cool. When sufficient water had been removed from the system, the mercury level in E was raised above Q to prevent any more vapour from escaping. The tap L was then opened to allow the water in the top of the mercury column to pass through, together with a small quantity of mercury. (With very low pressures the mercury did not rise as far as L.) L was then turned so that the tubes T, T₁, etc., were in connexion with M, and a current of dry air was pumped through so that all the water was conveyed to the tubes, which were then reweighed. This process was repeated until a sudden definite decrease in the pressure exerted by the contents of A was observed, after sufficient time had been allowed for equilibrium to be established. Water vapour was then slowly removed from A, a few bubbles at a time, until a new system resulted such that the withdrawal of a small quantity of

water vapour had no effect on the equilibrium vapour pressure at constant temperature, *i.e.*, the vapour pressure was that of a new pair of hydrates of boric anhydride. The pressure-temperature curve for this system was determined, thus giving curve II. The other curves in Fig. 2 and the losses in weight on passing from one part of the system to the other were determined similarly.

Several runs were necessary, for, in spite of its having been carefully annealed, the apparatus frequently broke, possibly owing to the fact that glass tends to be attacked by boric oxide at the higher temperatures employed. In no case was it found possible to continue until complete dehydration was effected. In the last run that was carried out, however, as much as 97.5% of the water present in the initial orthoboric acid was removed before the experiment had to be discontinued.

Table I shows the data from which the pressure-temperature curves were constructed. Pressures (p) were read to the nearest mm.; temperatures (t) were usually constant to at least 0.5° during the course of individual experiments and were subject to emergent stem corrections, which would normally act in the same direction, but were not applied. The thermometers were checked against Anschütz thermometers, with which they agreed fairly closely. No high degree of accuracy is therefore claimed for these measurements, which were made with the primary object of obtaining definite indications of equilibrium.

In the most complete run that was made, the initial weight of orthoboric acid was 5.4856 g. and the amounts of water lost to bring the system on the curves II, III, . . . IX, successively were:

>1.5855 <1.6591 g. (1.5926; $n = 1$)	>2.2295 <2.2331 g. (2.2296; $n = 5$)
>1.9835 <1.9925 g. (1.9907; $n = 2$)	>2.2541 <2.2577 g. (2.2562; $n = 6$)
>2.1201 <2.1267 g. (2.1234; $n = 3$)	>2.2663 <2.2753 g. (2.2751; $n = 7$)
>2.1863 <2.1923 g. (2.1898; $n = 4$)	>2.2753 <2.2929 g. (2.2893; $n = 8$)

The figures in parentheses show the calculated loss of weight for the formation of the hydrate indicated by the value of n in the formula $nB_2O_3 \cdot H_2O$. The existence of these compounds is confirmed by similar data in a previous experiment from HBO_2 as far as $6B_2O_3 \cdot H_2O$, at which stage the apparatus broke.

The calculated losses in weight of water are subject to corrections for the mass of water vapour contained in the bulb A; these corrections become smaller as the more dehydrated products form, with their relatively low vapour pressures, and are never large enough to invalidate the main conclusions.

To obtain the theoretically exact figures, a further correction would be necessary on account of the volatilisation of the boric anhydride component, of which there was evidence from the form-

TABLE I.

I. $B_2O_3, 3H_2O - B_2O_3, H_2O$.										
<i>t</i> ...	65°	75°	80°	89.5°	99.5°	109.5°	119.5°	129°	139°	
<i>p</i> ...	1.75	1.88	2.15	3.45	6.2	10.6	17.4	28.2	46.2	
<i>t</i> ...	144°	146°								
<i>p</i> ...	57.1	64.6								
II. $B_2O_3, H_2O - 2B_2O_3, H_2O$.										
<i>t</i> ...	130°	142°	146.5°	150.5°	157°	160°	162°	167°	172°	
<i>p</i> ...	3.0	4.9	6.2	7.8	11.35	14.5	16.95	25.7	39.25	
<i>t</i> ...	178°									
<i>p</i> ...	60.8									
III. $2B_2O_3, H_2O - 3B_2O_3, H_2O$.										
<i>t</i> ...	150.5°	157°	162°	163°	172.5°	173.5°	179.5°	183.5°	191°	
<i>p</i> ...	5.4	7.15	8.05	8.5	11.65	11.85	14.05	16.25	20.25	
<i>t</i> ...	192°	202.5°	204.5°	218°						
<i>p</i> ...	20.5	27.3	30.3	39.5						
IV. $3B_2O_3, H_2O - 4B_2O_3, H_2O$.										
<i>t</i> ...	150°	162°	171°	172.5°	179.5°	179.5°	190°	194°	201.5°	
<i>p</i> ...	2.3	3.25	4.1	4.35	5.65	5.75	8.1	9.7	11.4	
<i>t</i> ...	204.5°	211.5°	212°	219.5°						
<i>p</i> ...	13.05	15.4	15.8	20.0						
V. $4B_2O_3, H_2O - 5B_2O_3, H_2O$.										
<i>t</i> ...	154.5°	163°	168.5°	183.5°	184.5°	195.5°	203.5°	212.5°	212.5°	
<i>p</i> ...	1.5	1.95	2.2	4.35	4.7	6.0	7.8	9.9	9.5	
<i>t</i> ...	214°	220.5°	222°	231°	231°	242.5°				
<i>p</i> ...	10.0	12.6	13.6	17.4	17.5	24.5				
VI. $5B_2O_3, H_2O - 6B_2O_3, H_2O$.										
<i>t</i> ...	178.5°	189°	202.5°	206°	207.5°	211.5°	218°	220.5°	230°	
<i>p</i> ...	2.0	3.4	5.3	6.0	6.05	6.85	8.3	8.75	11.6	
VII. $6B_2O_3, H_2O - 7B_2O_3, H_2O$.										
<i>t</i> ...	180°	193.5°	205.5°	215.5°	217.5°	226.5°	231°	233°		
<i>p</i> ...	1.75	3.4	4.75	6.3	6.6	8.85	9.8	10.3		
VIII. $7B_2O_3, H_2O - 8B_2O_3, H_2O$.										
<i>t</i> ...	222°	230°	236°	241.5°						
<i>p</i> ...	5.8	7.3	8.5	9.9						
IX. $8B_2O_3, H_2O - B_2O_3(?)$.										
<i>t</i> ...	185°	197.5°	211.5°	226°	246°					
<i>p</i> ...	1.4	2.25	3.45	5.2	8.0					

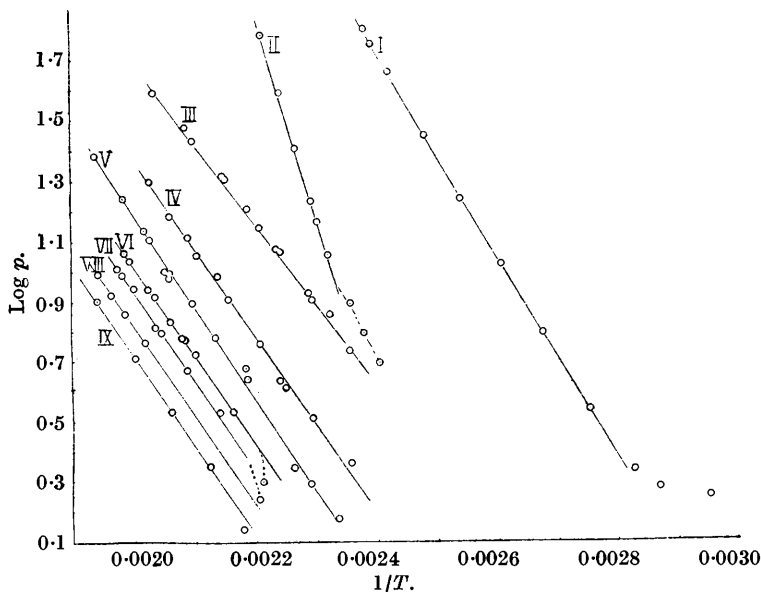
ation of a small quantity of a white deposit on the cooler parts of the tube QL, and also in T, but not in the exit tube of T. Most of this volatilisation seemed to occur when curves I and II were being examined. In one case when a breakage happened after 95.2% of the water had been removed, it was possible to obtain the contents of the bulb A in a clean state and to determine the boric oxide content, which was found to be more than 99% of that originally present. As most of this oxide condensed in the tube QL, it could retain relatively little water owing to the high temperature to which it was still subjected, and to the fact that it was in the form of a thin film which would facilitate the establishment of the boric

anhydride-water equilibrium. It does not appear, therefore, that the volatilisation of the boric anhydride component affects materially the data under consideration.

Curves I to VIII correspond therefore to equilibria between water vapour and the systems $B_2O_3, 3H_2O-B_2O_3, H_2O$; $B_2O_3, H_2O-2B_2O_3, H_2O$; . . . $7B_2O_3, H_2O-8B_2O_3, H_2O$.

It is not impossible that still lower hydrates of boric anhydride exist, but since, in the case in which 97.5% of the water was withdrawn, the vapour pressures exerted were still on curve IX, whereas the removal of 95.8 and 96.3% of water corresponds with the

FIG. 3.



formation of $8B_2O_3, H_2O$ and $9B_2O_3, H_2O$ respectively, it would seem that $9B_2O_3, H_2O$ cannot exist under our experimental conditions; if, therefore, curve IX does not represent the vapour-pressure curve for the system $8B_2O_3, H_2O-B_2O_3$, some hydrate lower than $9B_2O_3, H_2O$ is involved. Attainment of equilibrium is very slow, however, at this part of the system, and more data would be desirable.

A few measurements of the pressures exerted when orthoboric acid is heated at different temperatures are recorded by Lescoeur (*Ann. Chim. Phys.*, 1890, **19**, 35) and apparently belong to the system $3H_2O, B_2O_3-H_2O, B_2O_3$, as they are in rough agreement with our values for this system.

When the data of Table I are plotted as $\log p$ against $1/T$, Fig. 3

is obtained. It will be observed that the curves are approximately straight lines, with the exception of a few points at the lower temperatures (the deviations of which cannot be entirely explained). Hence the average approximate values of the heats of combination, Q , of the different hydrates (with one molecule of water vapour) can be calculated from the slopes of the lines by application of the equation $Q = 4.576 d \log p/d (1/T)$. The values of Q (in cal.) corresponding to the several curves are as follows: I, 15,600; II, 31,300; III, 12,300; IV, 13,300; V, 14,000; VI, 13,200; VII, 13,100; VIII, 13,500; IX, 13,300. From these are calculated the successive heat changes in the dehydration of orthoboric acid, as shown in Table II, the lowest hydrate capable of existence being assumed to be $8B_2O_3 \cdot H_2O$. On this assumption the heat of hydration of boric oxide to orthoboric acid is 54,363 cal.

Even if still lower hydrates exist, their contribution to the total heat of hydration would probably be small and of the same sign as in Table II. By subtracting the heat of vaporisation of three

TABLE II.

$B_2O_3 \cdot 3H_2O$	$\rightarrow B_2O_3 \cdot H_2O + 2H_2O$	- 31,200 cal.
$B_2O_3 \cdot H_2O$	$\rightarrow B_2O_3 \cdot \frac{1}{2}H_2O + \frac{1}{2}H_2O$	- 16,650 "
$\frac{3}{2}(2B_2O_3 \cdot H_2O)$	$\rightarrow \frac{3}{2}(3B_2O_3 \cdot H_2O) + \frac{1}{2}H_2O$	- 2,050 "
$\frac{3}{4}(3B_2O_3 \cdot H_2O)$	$\rightarrow \frac{3}{4}(4B_2O_3 \cdot H_2O) + \frac{1}{4}H_2O$	- 1,108 "
$\frac{1}{2}(4B_2O_3 \cdot H_2O)$	$\rightarrow \frac{1}{2}(5B_2O_3 \cdot H_2O) + \frac{1}{2}H_2O$	- 700 "
$\frac{1}{3}(5B_2O_3 \cdot H_2O)$	$\rightarrow \frac{1}{3}(6B_2O_3 \cdot H_2O) + \frac{1}{3}H_2O$	- 440 "
$\frac{1}{4}(6B_2O_3 \cdot H_2O)$	$\rightarrow \frac{1}{4}(7B_2O_3 \cdot H_2O) + \frac{1}{4}H_2O$	- 312 "
$\frac{1}{5}(7B_2O_3 \cdot H_2O)$	$\rightarrow \frac{1}{5}(8B_2O_3 \cdot H_2O) + \frac{1}{5}H_2O$	- 241 "
$\frac{1}{8}(8B_2O_3 \cdot H_2O)$	$\rightarrow B_2O_3 + \frac{1}{8}H_2O$	- 1,662 "

molecules of water (27,650 cal.), the value 26,700 cal. (approx.) is obtained, which can be compared with the values determined calorimetrically by Ditte (12,509 cal.; *Ann. Chim. Phys.*, 1878, **13**, 70) and by Berthelot (16,800 cal; *ibid.*, 1879, **17**, 133). As Ditte employed for his determination powdered boric oxide, which must have absorbed a large amount of water during its preparation owing to its exceedingly hygroscopic nature, the discrepancy between his value and ours is explained. Although Berthelot does not state the fact, it seems most likely that the boric oxide he used was also powdered, for the fused material dissolves only very slowly, probably far too slowly for such calorimetric methods as he was able to apply, and his determinations suffered, therefore, from the same error.

Summary.

Evidence is adduced for the existence of eight boric acids, $nB_2O_3 \cdot H_2O$, where $n = 1, 2, 3 \dots 8$. An approximate value for the heat of hydration of boric anhydride to orthoboric acid is

advanced, and differs considerably from previous data, which are shown to be probably inaccurate.

THE SIR WILLIAM RAMSAY LABORATORIES OF
INORGANIC AND PHYSICAL CHEMISTRY,

UNIVERSITY COLLEGE, LONDON. [*Received, December 13th, 1928.*]
