THE SYSTEM, WATER—BORON OXIDE.[1]

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ABSTRACT.

Measurements of the solubilities were made to establish the equilibrium relations over the whole range of compositions in the system composed of water and boron oxide.

The crystalline phases occurring in the system are found to be ice, H_3BO_3, three modifications of HBO_2 in monotropic relation to one another, and crystalline B_2O_3. Solubility curves have been determined for each of these phases, and the properties of the new phases are described. The P—T—X relations for saturated solutions were evaluated. These are of importance for geochemistry.

Boron oxide is a constituent of many minerals which occur in nature under conditions indicating widely differing modes of origin. Nearly all these minerals are attacked by aqueous solutions. The more soluble compounds occur in economically important quantities in salt beds and in desert lake and salt marsh deposits. Fumarolic and hot spring effluvia in many cases disengage large quantities of boric acid, not only in solution, but also in the vapor. Thus, in the suffioni of Tuscany, the steam issuing from the ground carries up to 0.5 g. of H_3BO_3 per liter at pressures reaching about 5 atm., the temperature being near 190° C. The boric acid is deposited here in the free state as the mineral sassolite, H_3BO_3. Because of the frequent occurrences of boron compounds in nature, the study of the heterogeneous equilibria in the system, $H_2O—B_2O_3$, is of direct interest for geophysical chemistry.

In industry, the most important use of boron oxide and its compounds, from the standpoint of heterogeneous equilibria, is in the ceramic and the glass industries, mainly as a constituent of certain special purpose glasses. Here the presence of B_2O_3 imparts toughness and other beneficial properties, such as low coefficient of expansion, and resistance to devitrification. The special character of the glasses derives from the unique prop-

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[1] Paper presented at the spring meeting of the American Chemical Society at Dallas, Texas, April 19, 1938.

erties of vitreous B_2O_3 and from its influence upon the properties of vitreous silica in the glass melts. Crystalline B_2O_3 is of interest here primarily for the reasons that its melting point is low, and that its crystallization is essentially a specialized process.

The published information on the equilibrium relations in this system is highly fragmentary. Aside from the ordinary boric acid, H_3BO_3, various other compounds have been reported, mostly on grounds that will not bear critical examination. Of these, the metaboric acid, HBO_2, is the only one for which a definite proof has been given. However, as we shall see, metaboric acid itself crystallizes in three modifications which stand in monotropic relation to each other; only two of these modifications appear to have been obtained before, and what is more important, without the realization that they were different crystalline phases. Further confusion arises from the failure of some workers to differentiate adequately between the amorphous and the crystalline states of matter. Until very recently, B_2O_3 has been known only in the vitreous condition, and hence, the various older statements concerning its "melting point" are obviously without meaning. The reason for many of these uncertainties lies in the fact that in many cases adequate criteria have not been employed to identify the crystalline products when obtained.

In working with the solutions in this system, there are encountered experimental difficulties which are more or less unique, and characteristic of the phases involved. At the higher B_2O_3 concentrations the solutions are highly viscous; the attainment of equilibrium is slow, not only for this reason, but also, and in greater measure, because of the inertness of behavior of some of the crystalline compounds in solution.

The work outlined in connection with this system at this Laboratory comprises the determination of the necessary data for the evaluation of the P—T—X relations, as far as may be practicable. The data presented in this paper include an experimental study of the solubilities for the entire range of compositions, and a correlation of these measurements with existing information on the vapor pressures, resulting in the evaluation of the vapor pressure relations for the saturated solutions. The optical and other properties of the various crystalline phases encountered are also given. Further work is in progress.

SOLUBILITY DETERMINATIONS.

The choice of method for the measurement of solubilities in this system is limited, for several reasons. Firstly, the vapor must be confined, since for most of the system, the vapor pressures at the liquidus are in excess of one atmosphere. Secondly, it is not practicable to separate the solution from the crystal phases by filtration, because the viscosities are generally too high. Thirdly, equilibrium is attained slowly for some of the phases, and hence, it is an advantage to follow the progress of the experiment visually. Finally, simplicity of method is desirable, when it can be secured without sacrificing accuracy.

For these reasons, we have employed the well known method of sealed tubes, in which solutions of known gross composition are heated at various temperatures, and a measurement is made of the temperature at which the last crystal dissolves in the saturated solution. The composition may be evaluated accurately from the weight of the constituents used, or by subsequent analysis.

The method has already been tested adequately in this Laboratory at elevated temperatures.[2] The apparatus for heating the sealed tubes consists of a copper-lined air bath thermostat whose temperature can be controlled with a precision of ± 0.02° C. at any temperature up to about 600° C. The thermostat is provided with windows for observation, and with means for circulating the air and rotating the solubility tubes to obtain efficient stirring of the contents. The temperatures are measured by calibrated thermocouples whose emfs. are read with the aid of a Wulf-Feussner potentiometer.

Pyrex chemical resistant glass tubes of 8 to 10 mm. internal diameter are used as containers for the solutions. The strength of such tubes is adequate to withstand the relatively low pressures developed by the vapor at the liquidus in this system, and the large diameter has the advantage of facilitating the stirring of the viscous solutions. The stirring may be further aided by adding gold beads to the contents of the tubes.

The principal objection to this method is the possibility of corrosion of the glass tubes. This was found to be negligible throughout the system, although slight etching was observed

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[2] Kracek, F. C.: J. Phys. Chem., 35, 417, 947, 1931; J. Am. Chem. Soc., 53, 2609, 1931; J. Wash. Acad. Sci., 26, 307, 1936.

with the highest B_2O_3 composition. On analysis it was found, however, that the impurities thus introduced amounted to less than 0.1 per cent.

TABLE I.

The system, H_2O-B_2O_3.

No.	% B_2O_3 Weight	Mole	Liquidus temp. °C. H_3BO_3	HBO_2III	HBO_2II	HBO_2I	B_2O_3	$(p/p_0)_1$
1	8.20	2.26	65.2	....	....	....	....	0.954
2	10.87	3.06	79.5	....	....	....	....	.935
3	15.51	4.53	99.7	....	....	....	....	.901
4	17.72	5.28	107.8	....	....	....	....	.883
5	20.66	6.31	117.1	....	....	....	....	.858
6	23.84	7.49	126.7	....	....	....	....	.830
7	27.48	8.93	136.3	....	....	....	....	.795
8	30.85	10.35	143.3	....	....	....	....	.761
9	35.03	12.24	151.5	....	....	....	....	.717
10	39.79	14.60	159.4	....	....	....	....	.663
11	44.01	16.90	163.4	....	....	....	....	.612
12	48.63	19.67	167.3	....	....	....	....	.553
13	49.15	22.10	169.8	....	....	....	....	.504
14	55.75	24.58	170.1	....	....	....	....	.456
15	56.30	25.00	171.1	....	....	190	....	.448
16	56.30	25.00	170.9	....	....	....	....	.448
17	56.30	25.00	171.0	....	....	190	....	.448
18	58.81	26.97	170.8	....	....	201	....	.413
19	61.14	28.93	169.6	....	....	212	....	.379
20	62.34	29.98	169.0	....	172.0	213	....	.361
21	65.84	33.27	166.1	....	181.3	219	....	.309
22	69.65	37.25	159.6	....	189.4	225	....	.252
23	71.31	39.13	....	....	192.5	227	....	.228
24	72.30	40.30	....	164.0	194.5	....	....	.212
25	75.05	43.76	....	....	198.0	232	....	.166
26	76.01	45.04	....	....	199.2	233	....	.153
27	76.98	46.38	....	173.5	200.0	234	....	.137
28	77.93	47.74	....	....	200.6	....	....	.123
29	79.45	50.00	....	176.1	200.9	....	....	.101
30	79.45	50.00	....	175.9	200.9	236	....	.101
31	79.45	50.00	....	175.9	200.9	....	....	.101
32	79.35	49.85	....	....	200.9	....	....	.102
33	79.40	49.92	....	....	200.9	235.6	....	.102
34	81.97	54.05	....	173.7	199.7	235	233	.069
35	83.75	57.14	....	170.0	197.5	231	253	.053
36	85.23	59.89	....	....	194.8	230	273	.040
37	86.66	62.69	....	159.5	....	....	....	.031
38	87.13	63.66	....	....	....	....	298	.028
39	87.65	64.74	....	....	....	....	303	.025
40	89.86	69.63	....	....	....	....	334	.016
41	92.36	75.78	....	....	....	....	363	.009
42	92.96	77.35	....	....	....	....	367	.007
43	95.31	84.01	....	....	....	....	392	.004
..	100.0	100.0	....	....	....	....	450	...

Reagents.

The compositions studied were made up quantitatively by enclosing in the sealed tubes known weights of the constituents. Although it would have been feasible to use the end components H_2O and B_2O_3 throughout the system as reagents, it was found preferable to use mixtures of H_3BO_3 with water, or with anhydrous B_2O_3 glass, depending upon the desired composition. In some cases HBO_2 was also used as reagent.

The H_3BO_3 was reagent grade boric acid further purified by recrystallization.

Anhydrous B_2O_3 glass was prepared by heating "boric acid anhydride," reagent grade, to 1300° C. Evaporation with HF, and with methyl alcohol and HCl mixture left a negligible residue in each case, indicating less than 0.05 per cent impurities.

Metaboric acid in a coarsely crystalline condition (HBO_2II, vide infra) was prepared by heating recrystallized H_3BO_3 at 130-140° C. for 2 or 3 days in vessels from which the escape of vapor was partially impeded. Analysis showed this to be generally 79.40 ± 0.05 per cent B_2O_3 ($HBO_2 = 79.45$).

The Solubility Relations.

The crystalline phases occurring at the liquidus in the system are ice, orthoboric acid (H_3BO_3), three modifications of metaboric acid (HBO_2I, II, III), and crystalline B_2O_3. The solubility curve for ice extends only from the freezing point of ice to the cryohydric point at —0.76° C., and needs no further consideration. Measurements have been made for all the other phases. The data are given in Tables I and II, and are graphically illustrated in Fig. 1.

TABLE II.

Invariant points, H_2O-B_2O_3.

Phase reaction	Mole % B_2O_3	Temp. °C.	$(p/p_o)_1$
Melting of ice	0.0	0.0	1.0
Eutectic ice + H_3BO_3	0.333	—0.76	0.994
Melting of H_3BO_3	25.00	170.9 ± 0.2	.448
Incongruent melting $H_3BO_3 \rightleftarrows HBO_2I$ + liqd.	21 ± 1	169 ± 1	.523
Eutectic H_3BO_3 + HBO_2II	29.3 ± 0.2	169.6 ± 0.2	.373
Eutectic H_3BO_3 + HBO_2III	38.0 ± 0.2	158.5 ± 0.5	.242
Melting of HBO_2I	50.00	236 ± 1	.101
Melting of HBO_2II	50.00	200.9 ± 0.5	.101
Melting of HBO_2III	50.00	176.0 ± 0.2	.101
Eutectic HBO_2III + B_2O_3	50.0 ± 0.5	176.0 ± 0.2	.101
Eutectic HBO_2II + B_2O_3	51.8 ± 0.5	200.5 ± 0.5	.086
Eutectic HBO_2I + B_2O_3	55.1 ± 0.5	235 ± 2	.063
Melting of B_2O_3	100.00	450 ± 2	.000

1. *The Solubility of Orthoboric Acid.* The properties of this compound which occurs in nature as the mineral sassolite are known in considerable detail, and its crystal structure has been determined.[3] It crystallizes in plates and prisms, and it dissolves readily with little tendency to form highly supersaturated or undersaturated solutions. The solubility has been studied from the cryohydric point to 120° C. by Nasini and Ageno,[4] Sborgi and Ferri[5] and others. Owing to the methods

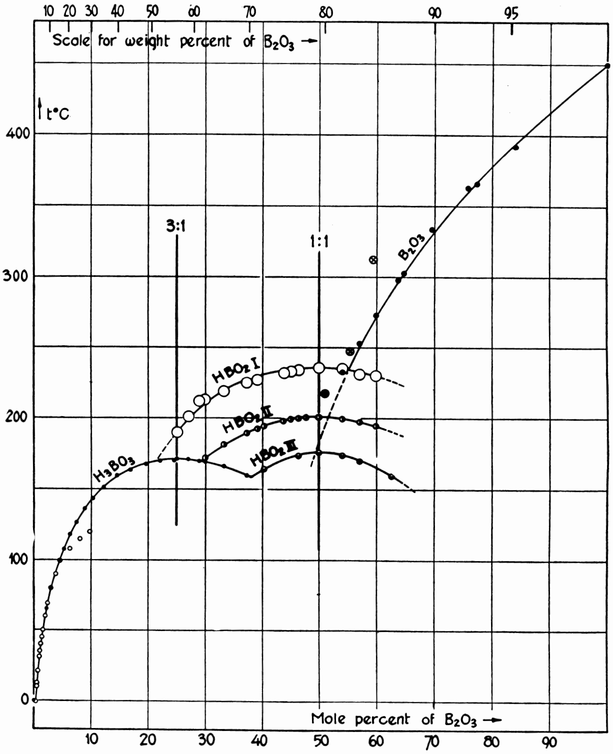

Fig. 1. Solubility diagram for the system, H_2O — B_2O_3. Open circles on and near curve for H_3BO_3, Nasini and Ageno; crossed circles near curve for B_2O_3, McCulloch; all other points by the authors. McCulloch's m. p. for B_2O_3, not indicated in figure, is 460-470°. The curve drawn for the solubility of B_2O_3 represents equation (1).

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[3] Zachariasen, W. H.: Z. Krist., 88, 150, 1934.

[4] Nasini and Ageno: Gazz. chim. ital. 41-I, 131, 1911.

[5] Sborgi and Ferri: Mem. accad. Lincei (5) 13, 586, 1922.

employed, the published data are not accurate above 100° C. Our results for the solubility of this compound yield a curve having a flat maximum at the melting point, 170.9° ± 0.2° C.[6] A part of this curve is metastable with respect to two of the forms of metaboric acid, discussed in the next section.

2. *The Solubilities and Crystallization of the Metaboric Acids* HBO_2I, HBO_2II, HBO_2III. Metaboric acid is capable of crystallizing in three distinct modifications with very different properties. This has been overlooked by previous workers, although the fact that the three phase pressures for the dissociation of H_3BO_3 to HBO_2 and water vapor, as measured by different authors, fall upon two separate P — T curves proves that two of these modifications at least should have been recognized. This will be discussed in detail at a later point.

As may be seen from the solubility diagram, the three modifications exist in monotropic relation to each other, their melting points being as follows: HBO_2I 236° ± 1° C., HBO_2II 200.9° ± 0.5° C., and HBO_2III 176.0° ± 0.2° C.

HBO_2III crystallizes almost as readily as H_3BO_3. The other two forms grow much more slowly, HBO_2I in particular being very inert in behavior.

When H_3BO_3 is dehydrated in open vessels at about 130° C., the dehydration product at first consists of flaky crystals of HBO_2III admixed with unconverted H_3BO_3; on continued heating the H_3BO_3 gradually disappears and the HBO_2III recrystallizes to coarsely crystalline HBO_2II. At this stage the dehydration stops promptly at the composition HBO_2 unless the time is excessive, or the temperature is raised above 150° C. Under these conditions the dehydration slowly continues, yielding a highly viscous liquid whose composition lies between HBO_2 and B_2O_3. As we shall see shortly, this liquid occasionally carries a more or less abundant quantity of the stable modification of metaboric acid, HBO_2I, and in some such cases may give rise to spontaneous crystallization of B_2O_3.

When the coarsely crystalline HBO_2II is melted in the sealed tubes, there usually remain in the liquid a few brilliant crystallites of HBO_2I. These grow with extreme reluctance, the complete crystallization of the contents of a tube requiring sometimes many weeks for completion. We have found no way to accelerate the growth; conversely, the dissolution of

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[6] Von Stackelberg, Quatram and Dressel, Z. Elektrochem., 43, 14, 1937, give 170° C. for the m. p. of H_3BO_3 and 203° C. for HBO_2.

this phase is also a slow process, the crystals being very slowly attacked by water at ordinary temperature. In consequence of this, it is possible to isolate the phase in pure form by leaching out the more rapidly soluble constituents of a mixture in which it occurs and collecting the crystals upon a filter. This was done for measurement of the density.

When sealed tubes containing melted HBO_2 are quickly cooled, the contents at first solidify to a glass, which then gradually becomes milky owing to the incipient crystallization of HBO_2III. On raising the temperature, the contents quickly crystallize to an opaque white mass which melts sharply at 176.0° C., the melting point of HBO_2III.

The recrystallization of HBO_2III to the more stable forms, HBO_2II or HBO_2I in sealed tubes, depends on the presence of nuclei of the more stable phases. Prolonged heating above 201° C. causes the melt to become sterile with respect to HBO_2II, and HBO_2III can then be kept unaltered in such tubes for indefinite periods. Prolonged heating at 170°-175°C. usually, however, results in recrystallization to HBO_2II, and in many cases also produces an abundant quantity of HBO_2I. It should be mentioned at this point that the HBO_2I, if completely absent originally, can be induced to crystallize in this way. On the other hand, heating HBO_2II in sealed tubes at just below its melting point does not tend to initiate the spontaneous growth of HBO_2I.

The compositions of the different modifications of metaboric acid were established by analysis, titrating weighed samples with a standard $Ba(OH)_2$ solution in the presence of mannitol, using phenolphthalein as indicator.

In the case of HBO_2III the method was an indirect one, being combined with the deductions from the solubility relations. Both the synthetic and the analyzed compositions representing HBO_2 gave the maximum liquidus temperature for HBO_2III, and particularly, determinations on solubility tubes filled with analyzed HBO_2II prepared by dehydration in open vessels yielded, after melting the HBO_2II, quenching, and recrystallization to HBO_2III, a homogeneous product which melted at 176.0 ± 0.2° C.

HBO_2II prepared by dehydration of H_3BO_3 in open vessels at 130°-140° C. was consistently found to be of nearly the theoretical composition, analyses giving 79.40 ± 0.05 weight per cent B_2O_3, as against the theoretical 79.45.

HBO_2I was prepared for analysis in sealed tubes. In this case, since there was a possibility that the crystals might be some other hydrate, such as $H_2B_4O_7$, the composition from which the phase was crystallized for analysis was chosen purposely to be different from HBO_2, being 80.2 weight per cent B_2O_3. After several weeks crystallization, the tubes contained a quantity of the desired crystals and some uncrystallized solution. The solution was drained off into one end, and the tubes were then cut open and the contents analyzed. The contents of the upper portion of the tubes were found to be 79.6 ± 0.1 per cent B_2O_3, i.e., practically pure HBO_2. The uncrystallized solution together with the crystals deposited in the lower portion always had a higher B_2O_3 content than the original 80.2 per cent B_2O_3 mixture, typical results being 80.8 and 81.2 per cent B_2O_3. The results of these analyses prove therefore that the crystalline phase in question has the composition of HBO_2.

The solubilities of the three modifications of metaboric acid are represented, as may be seen from Fig. 1, by three nearly parallel curves with flat maxima at the composition of the acid. The determination of the separate solubility curves, though tedious from the standpoint of the time involved, presents no particular difficulties. The most important precautions to observe are to make the stirring as efficient as possible, to give ample time for equilibrium to be attained, and especially in the case of HBO_2III, to keep the other two modifications from growing while the determination is being made. The time necessary for saturation with HBO_2III is short, 30 minutes to one hour being ample at each constant temperature even for the viscous solutions on the B_2O_3 side of the compound. With HBO_2II, saturation is obtained more slowly, but here also, the time required is not excessive. With HBO_2I, however, at least 48 hours must be allowed at each temperature, and even then, equilibrium is sometimes not certain in the more viscous solutions. Efficient stirring is of the utmost importance. The behavior of this phase in aqueous solutions is somewhat comparable in speed to that of crystalline quartz in alkali silicate melts, and may be more sluggish.

In solutions richer in B_2O_3 than HBO_2, the solubilities were determined over a moderate range of compositions in the region metastable with respect to crystalline B_2O_3. Determinations in this region are of interest for the reason that B_2O_3 tends to crystallize spontaneously from these solutions in the presence of crystals of HBO_2I.

3. *Crystalline Boron Oxide.* The phase which was later identified as crystalline B_2O_3 was first obtained in our solubility tube 38 (63.66 mole per cent or 87.13 weight per cent B_2O_3), made up from H_3BO_3 and anhydrous B_2O_3 glass. After dissolving the glass in the solution, the tube was set aside for several months at about 175° C. to crystallize. When crystals had developed, it was found that, in addition to the metaboric acids, there was present a new phase whose liquidus at this composition is 298° ± 1° C. At that time the solubility relations for the other phases were known only in outline; however, it was found that, in other experiments on the liquidus of what we now know to be HBO_2I in B_2O_3 rich solutions, the same phase usually began to precipitate before all the HBO_2I dissolved, and several points on its liquidus were determined at that time.

Later, this phase was isolated by settling and draining off the liquid. The material isolated was then used in seeding experiments, which furnished some very important information.

The seed was first added to anhydrous B_2O_3 glass, which was heated for several months at various temperatures. The results were completely negative, the added crystals merely remaining suspended in the softened glass in a wholly inert condition. This was also the case when the seed was added to glass containing about one per cent of water in a sealed tube; the seed melted when the temperature was raised to 430° ± 10° C.

On adding the seed to a mixture containing about five per cent of water in a sealed tube, a moderately rapid growth of crystals was observed, seemingly complete crystallization being obtained in 24 hours at 250° C.

When the seed was added to other compositions richer in water, relatively rapid crystallization took place, and the various points on the liquidus were then determined.

The seed was also added to HBO_2II in open crucibles. As soon as the metaboric acid began to melt, a gentle bubbling started, accompanied by a clouding of the melt, and in less than 24 hours the mass was changed to a rock-like aggregate of minute crystals cemented by a small quantity of glass.

The crystals used for seeding were comparatively well developed, and their optical properties were determined (vide infra). The crystals obtained in the open crucibles, and in the short-time experiments in sealed tubes, are extremely minute, and are unsuitable for examination. By X-ray diffraction, all these crystals were shown to be alike, and different from the other phases, and the preparations obtained in the open crucible experiments were analyzed. After 18 hours heating near 205° C. the B_2O_3 content was found to be near 99 weight per cent; after heating for more than 40 days at 400° C. the analysis gave 100.0 ± 0.1 per cent B_2O_3, with very little glass visible under the microscope.

Towards the end of our experimental work McCulloch[7] was the first to announce the spontaneous crystallization of boron oxide from partially dehydrated boric acid in open vessels. His results on large batches presented a new aspect of the problem for the reason that experiments on small batches analogous to his had always given us only a more or less dehydrated vitreous phase. On duplicating his procedure more or less closely, it was found at first that no crystallization of B_2O_3 was obtained except in one experiment out of a number. In this particular experiment it was noted that, as the dehydration proceeded beyond the HBO_2 stage, there remained a small incrustation of HBO_2I crystals on the walls of the container. When this deposit was mixed with the melt and heating was continued at 210° C., the melt clouded in a short time, and in 24 hours was found to be almost completely crystallized.

To confirm this observation we performed parallel experiments with two samples of HBO_2II which originally contained no HBO_2I, as determined by melting a separate sample in a sealed tube. To one of the samples was added a small quantity of HBO_2I; the other sample was used as control. The two samples were heated at 205° C. separately, to avoid any possibility of contamination. In the material with HBO_2I added, there was observed a clouding of the melt shortly after the HBO_2II melted, and in less than 3 days the sample was crystallized almost completely to B_2O_3. The control sample merely continued to dehydrate, with no crystallization in more than a week.

A final conclusive experiment was performed starting with recrystallized H_3BO_3. From the solubility relations we know that as the gross B_2O_3 content of the system exceeds that of H_3BO_3, the stable phases in coexistence at temperatures below the incongruent melting point of H_3BO_3 to HBO_2I and liquid are HBO_2I and H_3BO_3, up to the composition HBO_2. The other modifications of HBO_2 may also be present simul-

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[7] McCulloch, L.: J. Am. Chem. Soc., 59, 2650, 1937.

taneously, but that is non-essential. If the dehydration of H_3BO_3 is performed slowly, HBO_2I should be present, at least in small amounts. That is what is actually observed. The H_3BO_3 in this experiment was slowly dehydrated in a closely covered flask for a week at 120° C., after which the temperature was raised at 10° intervals daily to 200° C. At the end of this time the flask contained a viscous melt from which had settled out a relatively large quantity of HBO_2I crystals. The melt also showed a faint clouding, but crystallization was not proceeding at an appreciable rate, which is in accord with our experience, that B_2O_3 does not crystallize readily from highly dehydrated viscous melts. To reduce the viscosity, a roughly calculated quantity of the purified H_3BO_3 was added to bring the composition to near HBO_2, and heating was continued with the oven set at 200° C. In a short time the added H_3BO_3 was converted to HBO_2. When this melted, the previously observed clouding was found to increase at a rapid rate accompanied by quiet ebullition. The crystallization of B_2O_3 then completed itself in about 36 hours.

In all other experiments in which HBO_2I was totally absent, the dehydration resulted in a viscous melt with no crystallization, and in particular, we have never found HBO_2II or HBO_2III to initiate the spontaneous crystallization of B_2O_3, whether in open vessels, or in sealed tubes.

To recapitulate the results of our various experiments on the crystallization of B_2O_3, it may be stated that:

(1) the crystallization is not spontaneous in clear solutions;

(2) the crystallization has been initiated by crystals of HBO_2I (compare under properties of crystalline B_2O_3 below) but not by HBO_2II or HBO_2III;

(3) in sealed tubes it is initiated below the eutectic temperature for HBO_2I and B_2O_3, and growth seems to occur most rapidly when the liquidus temperature for HBO_2I is just slightly exceeded in the case of solutions somewhat richer in B_2O_3 than the eutectic, so that the crystals of HBO_2I are melting in the liquid;

(4) in open vessels the initiation occurs at these or lower temperatures, owing to the continuous dehydration of the melt and the consequent tendency toward dissociation of HBO_2I. The quadruple point (HBO_2I—B_2O_3—solution—vapor) pressure at the eutectic (235° C.) is calculated to be 1.9 atm., and the corresponding three phase pressure for the dissociation of

HBO_2I reaches 1 atm. in the neighborhood of 200° C. (see Figs. 3 and 4 and Table II);

(5) when the crystallization is initiated by seeding or by the presence of HBO_2I, the speed is relatively high in solutions or melts whose composition is near HBO_2, but becomes very small when the composition is near B_2O_3. The viscosity of the solutions changes enormously over this range of composition, and may account for some of the observed reluctance towards crystallization from high B_2O_3 concentrations. It is problematical whether it accounts for all of it, and in this connection, Zachariasen's picture of the constitution of B_2O_3 glass[8] is suggestive. It is reasonable to assume that the extended networks of atoms characteristic of the vitreous oxide are more limited in extent and more easily subject to rearrangement in the more highly hydrated melts or solutions near HBO_2 than in the anhydrous condition.

From the above discussion it is easy to see that the spontaneous crystallization of B_2O_3 is not a simple process, depending as it does on the previous formation of HBO_2I. The saving feature in the process is that HBO_2I is capable of existence over a very great extent of the system, and that its nucleation presents no particular difficulties.

The melting point of B_2O_3 was determined by the method of quenching, as used in this Laboratory for the study of phase equilibria in silicate systems. The value obtained is 450° ± 2° C., 3 days being allowed at each temperature for the attainment of equilibrium. The absence of crystals was determined microscopically. The value obtained is lower than McCulloch's 460°—470° C., but is in essential agreement with it, as contrasted with the previously reported value of 294° C. by Cole and Taylor.[9] The material employed in our determination had been crystallized in a platinum crucible for more than 40 days at 400° C. and was found by analysis to be 100.0 ± 0.1 per cent B_2O_3. The crystallized material carried only a small quantity of glass.

The solubility determinations in sealed tubes were not extended beyond 95.31 weight (84.01 mole) per cent B_2O_3, for two reasons. One was that beyond this point it becomes increasingly more difficult to stir the solutions because of the extremely high viscosity at the liquidus, so that there can be no

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[8] Zachariasen, W. H.: J. Am. Chem. Soc., 54, 3841, 1932.

[9] Cole and Taylor: J. Am. Ceram. Soc., 18, 55, 1935.

assurance of equilibrium having been reached; the second reason was that a slight corrosion of the tubes is observed at this and higher concentrations of B_2O_3, and it was felt that points determined in the remaining region would be of uncertain accuracy.

The solubility values for B_2O_3 fall on a curve represented by the empirical equation

$$(1)\quad \log N_2 = \frac{119.1}{4.574\,T} - 1.700 \log T + 0.002485\,T + 3.0278$$

where N_2 is the mole fraction of B_2O_3 for H_2O and B_2O_3 as components, and T is the Kelvin temperature. On applying deductions from Gibbs' method of dealing with heterogeneous equilibria, the slope of this curve yields

$$(2)\quad \Delta H = 2.303\,T \left(\frac{d \log N_2}{dT}\right) \left(N_2 \frac{d\mu_2}{d N_2}\right)_{p,\,T}$$

$$(2')\quad \Delta H = 2.303\,RT^2 \left(\frac{d \log N_2}{dT}\right) \left(\frac{d \log a_2}{d \log N_2}\right)_{p,\,T}$$

which, on introducing numerical values, becomes

$$(2'')\quad \Delta H \Big/ \left(\frac{d \log a_2}{d \log N_2}\right)_{p,\,T} = -\,119.1 - 3.376T + 0.011364T^2$$

$$= 3380 \text{ cal./mole at } 723^\circ\text{K} \quad (450^\circ \text{ C.}).$$

In the above equations μ_2 and a_2 are the chemical potential[10] ("partial molal free energy" of Lewis) and the activity of B_2O_3 (standard state $N_2 = 1$) in solution, and ΔH is the differential heat of solution of crystalline B_2O_3. Since we have no experimental data as yet for ΔH or μ_2 as functions of the concentration, it is at present impossible to evaluate the two quantities separately.

If the solubilities are expressed in terms of N_2', N_2' being the mole fraction of B_2O_3 with HBO_2 and B_2O_3 as components, the plot of log N_2' against $1/T$ is a straight line over a

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[10] We employ μ_i in the sense defined by Gibbs, as the chemical potential per unit mass of component i, which in this case is the mole. μ_i is then identical with Lewis' $\bar{F}_i$ or Guggenheim's $\bar{G}_i$ when P, T, and N are the variables.

wide range of compositions (from $N_2' = 0.3$ to 1.0). From the slope of this line we obtain

$$(2''') \qquad \Delta H \Big/ \left(\frac{\mathrm{d}\log a'_2}{\mathrm{d}\log N'_2}\right) = 2.303\,RT^2 \left(\frac{\mathrm{d}\log N'_2}{\mathrm{d}T}\right)$$

$$= 6720 \text{ cal./ mole,}$$

or, in round numbers, 97 cal./g., a value almost exactly double that obtained from equation (2″) at the melting point. This is the heat of fusion of B_2O_3 calculated on the assumption that $a_2' = N_2'$, that is, that Raoult's law holds in terms of N_2' over the region for which the curve is a straight line. The assumption appears to be a reasonable one, and on its basis it follows that $a_2 = k_2N^2_2$, $a_1 = k_1N^2_1$ at the neighborhood of $N_2 = 1$, k_1 and k_2 being constants determined by the choice of standard state. This is of use in connection with the vapor pressure data, as we shall see shortly.

The calculated heat of fusion of B_2O_3, 97 cal./g., is large, the corresponding entropy of fusion being 9.3 entropy units per mole, a value about twice that for the melting of ice. We hope to have an experimentally measured value in the near future.

THE VAPOR PRESSURE RELATIONS.

It is well known that the boric acids are somewhat volatile.[11] The distribution of the components between the solution and vapor is such, however, that the partial pressure of B_2O_3 (or, of the acids) in the vapor is small in comparison with that of water, and hence, for purposes of calculation, the error introduced by assuming the total pressure to be equal to the partial pressure of water is relatively small.

The activity of water, a_1, in the saturated solutions of a given binary system may be expressed by

$$(3) \qquad \frac{\mathrm{d}\ln a_1}{\mathrm{d}T} = \left(\frac{\mathrm{d}\ln a_1}{\mathrm{d}T}\right)_X + \left(\frac{\mathrm{d}\ln a_1}{\mathrm{d}X_1}\right)_T \left(\frac{\mathrm{d}X_1}{\mathrm{d}T}\right)_p$$

On comparing this with the expression derivable on the basis

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[11] Von Stackelberg, Quatram and Dressel (op. cit.) contribute an extensive discussion on this question.

of Gibbs' theory of heterogeneous equilibria (second component non-volatile),

$$(3') \quad RT^2 \frac{\mathrm{d}\ln a_1}{\mathrm{d}T} = (H''_0 - H'')_1 + \frac{X'''_1 - X''_1}{X'_1 - X''_1}(H' - H'')_s$$

(accents relate to phases, subscripts to components), it is seen that the first term of (3) contains the heat of dilution of the solution by the addition of the liquid solvent, and that the second term contains the much larger heat of solution of the crystalline solute.[12, 13]

The heat of dilution is usually small, and its contribution in influencing the vapor pressure of a solution of a given concentration is small enough to have given rise to the generalization known as von Babo's law. In exact measurements its effect is perceptible, and normally must be taken into consideration.

Confining the attention to the second term of equation (3), and comparing with (3′), we see that if the solubility is known as a function of the temperature, and if the activity or the vapor pressure is known as a function of the concentration at various temperatures, then the correlation of the pressure—temperature—concentration relations of saturated solutions may be evaluated. For an accurate correlation the heats of dilution are needed, as was pointed out in the preceding paragraph; if they are not known, the calculation will still be correct in principle, but will be numerically somewhat inaccurate.

In the case of the system H_2O—B_2O_3, no heats of dilution are available, and the data upon which to base the vapor pressure-composition relations are also very incomplete. Enough is known, however, to make a simplified calculation which turns out to be accurate to probably somewhat better than ± 2 per cent in the activity values for the major part of the system. Throughout this calculation we are dealing with $(p/p_0)_1$ values uncorrected for deviations from the ideal gas, since such refinements would be totally unjustified. In the text we use the

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[12] X_i is generalized concentration. When the unit mass is the mole, as in equation (3′), $X_i \equiv N_i$, the mole fraction of component i.

[13] Equation (3′) is obtained by subtracting $RT^2 \, \mathrm{d} \ln p_0/\mathrm{d}T = (H''' - H'')_0$, for the pure volatile component from the corresponding expression for the three phase S — L — V pressure (compare e.g. Commentary on the Scientific Writings of J. Willard Gibbs, Yale University Press, New Haven, vol. 1, article by Morey, p. 243, equation 8), suitably rearranged in terms of $RT = pv'''$, $H = ST$ ($\equiv \eta t$ of Gibbs) and neglecting the volume per mole of the condensed phases in comparison with that of the vapor phase.

symbol for the activity, a_1 in place of the vapor pressure ratio, as an abbreviation. The concentration is expressed in mole fractions of H_2O and B_2O_3 as components.

The older literature on the subject is summarized to 1924 in Mellor's Treatise,[14] and to 1926 in Gmelin's Handbuch.[15] Since 1926 work has been done by Gilbert and Levi,[16] Bezzi,[17] Menzel, Schulz and Deckert,[18] Thiel and Siebenbeck,[19] and by von Stackelberg, Quatram and Dressel.[20] The latter sketched in an approximate P — T diagram for parts of the system.

The pressure-composition (P — X) relations in this system are typical of many aqueous solutions of inorganic substances, exhibiting relatively high negative deviations from Raoult's law at high concentrations of the solute. At the aqueous end the a_1—N_1 curve starts out with a slope of 2, which is equivalent to Raoult's law being valid when the concentration is expressed in terms of H_2O and H_3BO_3 as components. In this region, measurements have been made by Tammann, Gerlach, Kahlenberg, Skirrow, and others, up to the composition of the saturated solution at the normal boiling point. For higher concentrations, there are available no direct measurements of the vapor pressures of solutions of accurately known compositions. We have made use of the three phase (S_I — S_{II} — V) pressure data of Gilbert and Levi, Lescoeur, Bezzi, Menzel and coworkers, and Thiel and Siebenbeck for the dissociation of orthoboric acid to metaboric acid and water vapor, in combination with the location of the corresponding quadruple points from the solubility data.

These three phase pressure data fall on two separate curves. Bezzi's results must be for dissociation to HBO_2II. They can be represented with good approximation by the Nernst type equation

$$(4) \qquad \log p_{mm} = \frac{-12350}{4.574T} + 1.75 \log T + 4.8115,$$

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[14] A Comprehensive Treatise on Inorganic and Theoretical Chemistry, by J. W. Mellor: Longmans Green and Co., London and New York, vol. 5, 1924.

[15] Gmelins Handbuch der anorganischen Chemie, 8. Auflage, Verlag Chemie, Leipzig and Berlin, System Nummer 13, 1926.

[16] Gilbert and Levi: J. Chem. Soc., 527, 1929.

[17] Bezzi, S.: Gazz. chim. ital., 65, 766, 1935.

[18] Menzel, Schulz and Deckert: Z. anorg. allgem. Chem., 220, 49, 1934.

[19] Thiel and Siebenbeck: Z. anorg. allgem. Chem., 220, 236, 1934.

[20] Von Stackelberg, Quatram and Dressel: Z. Elektrochem., 43, 14, 1937.

which yields for the heat of dissociation (with the evolution of water vapor) the value

(4′) $$\Delta H_{DII} = 12350 + 3.475\,T.$$

The eutectic composition for the coexistence of H_3BO_3 and HBO_2II (169.6° C.) combined with equation (4) yields

(4″) $$a_1 = 0.373,\ N_1 = 0.707\ (N_2 = 0.293).$$

The measurements of Gilbert and Levi (their series I), Lescoeur, and of Menzel and coworkers must represent the dissociation of H_3BO_3 to form HBO_2III, and yield the equations

(5) $$\log p_{mm} = \frac{-13940}{4.574\,T} + 2\log T + 4.8254,$$

(5′) $$\Delta H_{DIII} = 13940 + 3.972\,T,$$

which combined with the location of the eutectic for H_3BO_3 and HBO_2III (158.5° C.) yields

(5″) $$a_1 = 0.242,\ N_1 = 0.620\ (N_2 = 0.380).$$[21, 22]

Gilbert and Levi's series II will be referred to at a later place. Their series III to IX obviously represent data for unsaturated solutions, but it is not clear what the exact compositions were. Their own explanation of these results in terms of various polyboric acids is untenable, but the data are of value in indicating, at least roughly, the course of the $a_1 - N_1$ curve in the region of high B_2O_3 concentrations.

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[21] The coefficient of log T in (5) was made equal to 2 in round numbers to bring the values of the vapor pressure constant in equations (4) and (5) to approximately the same value.

[22] It is of interest to note that the transformation of HBO_2III to HBO_2II must have occurred during Thiel and Siebenbeck's measurement of the dissociation pressure at 100° C. They remark: "Charakterisch ist die ausserordentliche Langsamkeit, mit der sich das Gleichgewicht uber reiner Orthoborsaure als Ausgangssubstanz ausbildet. Noch nach 120 Stunden Versuchsdauer ist der stabile Endwert nicht erreicht." From their context it is evident that the pressure was rising, as it should in the case of the above-mentioned transformation. The sluggishness of the process could only be due to the slowness of the conversion rather than to any necessary lack of equilibrium of the vapor with the solids present, since neither Bezzi, nor Gilbert and Levi nor Lescoeur had any pronounced difficulties in establishing equilibria.

The derived pressure-composition relations are represented in Fig. 2, by plotting $(p/p_0)_1 = a_1$ against the concentration N_1 of water in mole fractions of H_2O and B_2O_3. By trial it was found that a useful deviation curve could be constructed by plotting $a_1^{1/3}$ against N_1.

At the aqueous end, as already stated, the solutions approximately obey Raoult's law for H_2O — H_3BO_3. Curves A and $A^{1/3}$ represent the expected course of the curves on this basis.

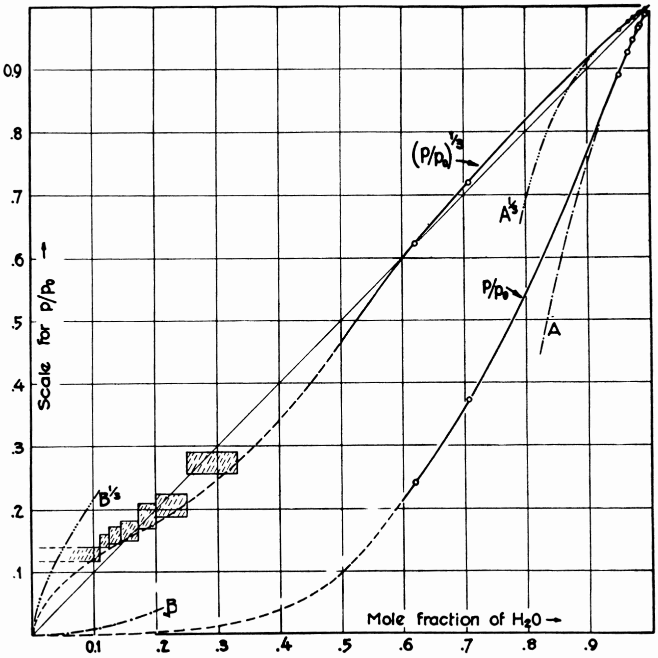

Fig. 2. Relative vapor pressure and composition relations for H_2O — B_2O_3 solutions. For explanation consult the text.

At the B_2O_3 end we have assumed that the $a_1 - N_1$ curve starts out in accord with Raoult's law for HBO_2 and B_2O_3 as components, on the basis that the melting curve of crystalline B_2O_3 (vide supra) yields a straight line of log N_2' against $1/T$. Curves B and $B^{1/3}$ represent the expected course of the curves on this basis, which requires that a_1 be proportional to N_1^2. Actually, at the present state of our knowledge of the vapor pressure relations, the point is of minor importance in our calculations, but the fact that the theoretical curve runs in the neighborhood of the location of the shaded rectangles representing Gilbert and Levi's series III to IX lends support to the basis of our calculation of the heat of melting of B_2O_3.

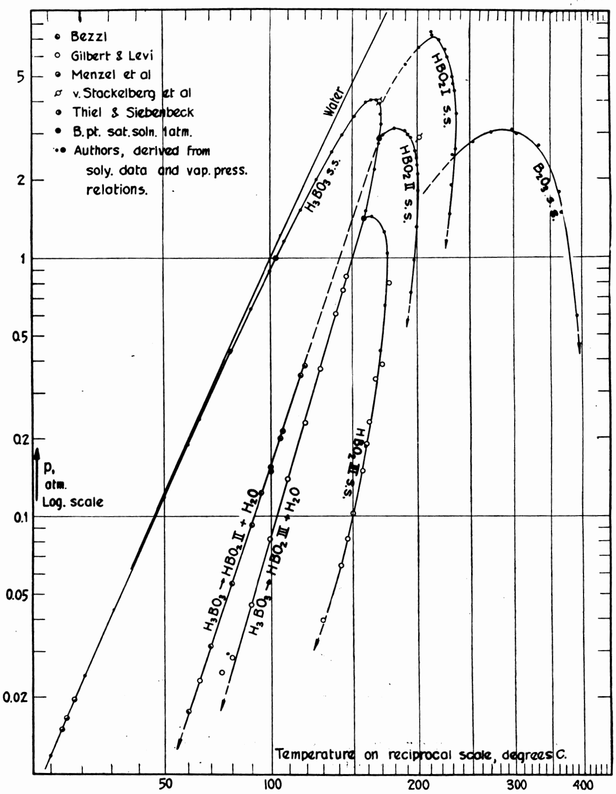

Fig. 3. P — T diagram for the vapor pressures of saturated solutions in the system, H_2O — B_2O_3.

From the curves of Fig. 2 and from the solubility data of Fig. 1, the P — T relations for the saturated solutions were evaluated as shown in Figs. 3 and 4. The $a_1 = (p/p_0)_1$ values from Fig. 2 are also given numerically as part of Tables I and II.

The accuracy of the calculated P — T relations in Figs. 3 and 4 may now be estimated by comparison with direct experimental data from the literature.

Menzel and coworkers measured the vapor pressures of saturated solutions of H_3BO_3 at 13.5°, 15° and 17.5° C., obtaining 11.4, 12.6 and 14.8 mm. Hg. The calculated values at these temperatures are 11.48, 12.65 and 14.80 mm. Hg., the solubilities being 0.58, 0.61 and 0.66 mole per cent B_2O_3, respectively.

The calculated curve is accurate by construction at the boiling point of the saturated solution, 103.2° C. The solubility at this point is 4.86 mole per cent B_2O_3.

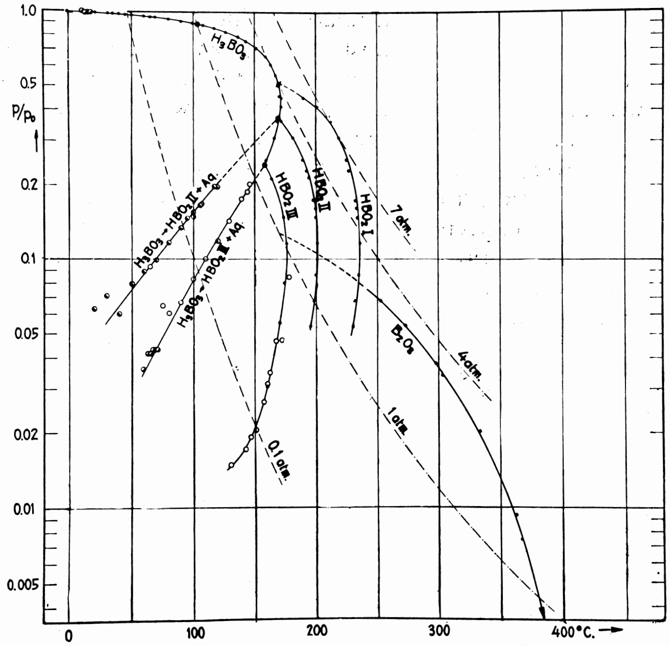

Fig. 4. Relative vapor pressure and temperature relations for the saturated solutions in the system, H_2O — B_2O_3. Experimental points are marked same as in Fig. 3.

Von Stackelberg and collaborators measured roughly the vapor pressure for melting H_3BO_3 at 170° C., 4.0 atm. ($a_1 = 0.51$), for melting HBO_2 at 203° C., 2.9 atm. ($a_1 = 0.18$), and for a composition given as 2g. H_3BO_3, 1g. HBO_2 (equivalent to 31.5 mole per cent B_2O_3), 168° to < 190° C., 3.9 atm. The calculated value of a_1 at 25.0 mole per cent B_2O_3, the composition of H_3BO_3, is 0.448 (see Tables I and II) as compared with the above measured value of 0.51. Actually the liquidus curve for H_3BO_3 passes through $a_1 = 0.51$ at approximately 169.7° C., the corresponding composition of the solution being about 22.0 mole per cent B_2O_3. When we remember that this is a dissociating compound[23] and that any solution that will be first formed will tend to be an unsaturated solution, the agreement is all that could be desired. In the case of the second point measured by these investigators, the agreement is not quite so fortunate. The calculated value of a_1 at the composition HBO_2 is 0.101, as against their reported value 0.18, which would correspond to a solution of about 43 mole per cent B_2O_3. The measurement was made at 203° C., which is above our melting point of HBO_2II, which obviously was the phase present. However, it must be pointed out that this phase requires a considerable time to come to equilibrium with its solutions, and it is to be expected that the first solution formed will be a water-rich solution rather than otherwise, for the same reason that was advanced in the case of H_3BO_3. The method employed was an ingenious one, but there is some question whether sufficient time was given to reach equilibrium. Thus, in the case of the third point reported by these workers, the pressure could not have remained fixed over the reported range of temperature if the composition given is accurate. The liquidus for HBO_2II at the given composition is 176° C., calculated $a_1 = 0.335$, which yields 3.02 atm. at the liquidus. Beyond this temperature the solution would be unsaturated, and would exert the reported vapor pressure of 3.9 atm. at just above 187° C. Their upper temperature, $< 190°$ C., may have been near this value.

The last measurements to be considered as a check on the calculations are those of series II of Gilbert and Levi. Reference to Figs. 3 and 4 shows that the average curve through their experimental points forms a continuation of the calculated curve for HBO_2III. The measured and the calculated portions of this curve agree to within $\pm$ 0.5 per cent in the activity values. It should be mentioned that the measurements of this series were not, and could not be, used in establishing the pressure-composition relations, since the composition of the solution was variable, owing to the presence of the solid phase. From the correlation it would appear that the composition in the apparatus must have been just over 50 mole per cent B_2O_3.

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[23] See for example, F. E. C. Scheffer, Z. physik. Chem. 71, 214, 671, 1910; A. Smits, ibid. 67, 455, 1909.

Since we have made the explicit assumption of von Babo's law in these calculations, it must be expected that in certain regions of the diagram the calculated P — T — X relations will be somewhat inaccurate. Another source of error lies in neglecting the contribution to the vapor pressure due to the presence of boric acids in the vapor phase. The error due to this factor is, however, of secondary importance. The calculated diagram is correct in principle, and as we have seen, in moderately good numerical agreement with fact throughout the relatively enormous region of compositions described.

It will be noted that the vapor pressures of solutions saturated with the various phases pass through maxima, located in each case on the H_2O side of the composition of the phase in question. The most interesting feature is that crystalline B_2O_3 can exist in equilibrium with solutions which exert a considerable vapor pressure. The vapor pressure maximum is located at about 280° C., being somewhat less than 3 atm. The corresponding composition of the saturated solution is about 62 mole per cent B_2O_3. It will be recalled that in many of the recorded unsuccessful attempts to crystallize this compound, the work was done on the anhydrous vitreous oxide, a region of composition which is particularly unsuitable for accomplishing the desired end. Another interesting point which arises in connection with the vapor pressure relations is that as the composition approaches 100 per cent B_2O_3, the aqueous pressures decrease to very low values (compare Fig. 2). This explains the observed difficulty of completely dehydrating the substance at moderate temperatures.

The Liquid-Vapor Composition Relations.

The experimental data now available on the volatility of boric acid from its solutions cover a comparatively narrow range of compositions, extending only up to the saturated solution at the normal boiling point. It is planned to extend this range by working at higher temperatures; in the meantime, it seems worth while to review the data already available.

The results of von Stackelberg and coworkers, on recalculation to mole fractions of H_2O and B_2O_3, may be expressed by

$$(6) \qquad \left(\frac{N_1}{N_2}\right)_{\text{vapor}} = (280 \pm 20) \left(\frac{N_1}{N_2}\right)_{\text{liquid}}$$

while those of Bezzi (and Skirrow) depart rather widely from the above, being best expressed by

$$(7) \qquad \left(\frac{N_1}{N_2}\right)_{\text{vapor}} = 550 \left(\frac{N_1}{N_2}\right)^{0.63}_{\text{liquid}}$$

over approximately the same range of composition.

The data of von Stackelberg et al. on the volatility of crystalline H_3BO_3 and HBO_2 in steam lead to the view that as the concentration of B_2O_3 greatly increases in the solution, the distribution coefficient will change in the direction in which the vapor will be relatively impoverished in B_2O_3. This is to be expected also on the basis of our limited knowledge of the volatility of vitreous B_2O_3. Accordingly, the distribution coefficient in equation (6) should rise with increasing concentration of B_2O_3 in solution.

A further numerical discussion of this question at this time would serve no useful purpose. The problem is of some importance in volcanology, and especially, in the study of the origin of the vapors rich in boric acid, which arise from steam vents and from steam wells in the hot spring regions of Italy, and elsewhere.

PROPERTIES OF THE CRYSTALLINE PHASES.

We have measured the density, the optical, and the crystallographic properties of all the new compounds prepared in this study, with the exception of the crystallographic properties of crystalline B_2O_3, which could be prepared only in microscopic crystals. We have also taken the opportunity to add to the known observations on H_3BO_3 (sassolite).

Sassolite, H_3BO_3, has been described by several observers. Further details of twinning, cleavage, flexibility, and optical properties of artificial crystals are presented here.

Microscopically, the triclinic crystals are tables with six 120° angles, bounded by *a*{100}, *p*{110}, *q*{1$\bar{1}$0} of Haushofer's orientation, or prisms with the axis oblique to the base 15°. Besides the eminent basal cleavage, a poor cleavage develops parallel to the *a*-axis when basal plates are flexed repeatedly about that axis. Resistance to such flexing is decided, but about the *b*-axis the plates flex with extreme ease, while a set of twinning lamellae develops, which outcrops on the base at an angle of 10° ± 2° to the *b*-axis and of 50° ± 2° to *p*. Many prismatic crystals of megascopic size were found twinned according to the albite law, with the twinning and composition plane $b\{010\}$.

Microscopically extinctions are nearly parallel to the base (see below) and in the prism zone the maximum extinction angle, that is, $\alpha \wedge c$, is 16°.

On the base the optic axial plane makes an angle of 17° ± 2° with $a\{100\}$ and of 43° ± 2° with $q\{1\bar{1}0\}$, and from measurements on the interference figures the acute bisectrix, α, is inclined 2° from the normal to the base toward $p\{110\}$. $-2V = 10°$, $-2E = 15°$. The refractive indices are $\alpha = 1.337$, $\beta = 1.461$, $\gamma = 1.462$.

Metaboric Acid HBO_2III. The crystals examined for optical and crystallographic properties were grown by deposition from the vapor phase: orthorhombic prism and base; tabular parallel to the base, or stubby prisms; interior prism angle measured microscopically 78½°. No better value was obtained goniometrically from the best available crystals with hydrated surfaces. Cleavage is so easy, parallel to the base, that slight pressure causes shearing of a crystal into many thin flakes. The optic axial plane bisects the acute angle of the prism. $-2V = 23°$ without noticeable dispersion, and with α, the acute bisectrix, normal to the base. Refractive indices are $\gamma = 1.521$, $\beta = 1.514$, α, in hexane, is less than 1.376. The crystals react rapidly with acetone, methyl alcohol, and acetonitrile.

The density was measured on crystals prepared in sealed tubes by quenching melted HBO_2 and recrystallizing the glass at 160° C. for 2 hours. The material was microcrystalline, but contained no HBO_2II or HBO_2I. The value obtained, 1.78, was measured in a pycnometer with toluene as the displacement liquid, after evacuation to remove the air.

Metaboric Acid HBO_2II. The holohedral monoclinic crystals from the vapor have a slightly elongated lenticular aspect, with the broad bulging front pinacoid rounded by two pyramids and a dome, to a small base. A very perfect basal cleavage meets a less perfect orthodomal cleavage $\{\bar{1}01\}$ at an interior angle of 86½°. The optic axial plane is $\{010\}$; $\gamma \wedge c$-axis $= 5_r°$, $4\frac{1}{2}_b°$ in acute angle β; $-2V = 35_r°$, and $36_b°$. The refractive indices $\alpha = 1.434$, $\beta = 1.570$, $\gamma = 1.588$; and the axial ratios $a : b : c = 0.81 : 1 : 1.78_0$ have been obtained as preliminary values on rough crystals with surfaces slightly altered by hydration. The observed angles, according to two-circle goniometry, are:

Forms		ϕ	ρ
c	001	90°	30½°
d	111	60	74½
e	012	35½	47½
g	$\bar{1}11$	48	69

The density, measured in a pycnometer on coarsely crystalline material resulting from dehydration of H_3BO_3 at 130° C. was 2.044 ± 0.003. The composition of the crystals was 79.40 ± 0.05 per cent B_2O_3.

Metaboric Acid HBO_2I. The most stable form of metaboric acid crystallizes as rhombic dodecahedra, and has the refractive index 1.619.

The density was measured both by flotation in a heavy liquid and in a pycnometer. The results agree closely, being 2.487 and 2.485, respectively, each ± 0.003. The crystals were grown in sealed tubes.

Crystalline Boron Oxide, B_2O_3. The largest crystals (diameter about 0.05 mm.), prepared by crystallization in solution in a sealed tube for about eight months, had the aspect of rhombohedra, and each contained a nucleus of a dodecahedral crystal of metaboric acid HBO_2I. Marked parallelism between the edges—and probably the faces—of the two were seen, but no definite crystallographic relationship could be established, because strain birefringence, and other irregularities in refractive index obscured the optical relationships. However, the crystals are nearly or quite uniaxial, with ω (or β and γ) $= 1.64_8$ and ϵ (or α) $= 1.61_5$. Crushing either induces a minute lamellar twinning, or possibly reveals a twinning caused by an inversion.

Crystals of B_2O_3, which are grown only a short time in solution, or produced by crystallization of the melt, are very minute. For measurement of the density, the crystals were prepared by crystallizing a seeded melt. The composition was 100 ± 0.1 per cent B_2O_3. The density is 2.460 ± 0.010, measured in a pycnometer.

The powder diffraction pattern for crystalline B_2O_3 was obtained for us by C. J. Ksanda of this Laboratory. This pattern was found to be in good agreement with that reported by McCulloch, but different from that of Cole and Taylor.

The determination of the crystal structures of the new crystalline phases has been kindly undertaken by W. H. Zachariasen, who will report his findings separately elsewhere. We are privileged to state at this time that his results agree with ours on the symmetry of HBO_2I and HBO_2II, as follows:

The structure of HBO_2I is cubic, $a_0 = 8.87_9$ Å with an accuracy of 0.1 per cent. This, combined with the density value of 2.486 yields 24 molecules of HBO_2 per unit cell.

The monoclinic unit cell of HBO_2II has the dimensions $a = 7.12$ Å, $b = 8.86$ Å, $c = 6.85$ Å, angle $\beta = 93° \, 30'$. The axial ratios $a:b:c$ are $0.803_6 : 1 : 0.773_1$, as contrasted with the crystallographic (vide supra). The X-ray cell transformed to the crystallographic orientation yields $a:b:c = 0.803_6 : 1 : 1.785$, angle $\beta = 59° \, 48'$. There are 12 molecules of HBO_2 per unit cell, and the space group is probably C_{2h}^5.

DISCUSSION.

In the preceding pages we have already discussed the equilibrium relations between the various phases in some detail, and have pointed out some of the more important features of this investigation, together with its bearing on the work of this Laboratory. It remains to mention some of the problems which remain to be studied, and some conclusions that may further be drawn from the work already completed.

It should be emphasized that B_2O_3 is a unique substance. In its vitreous form it is tough rather than brittle, and this property appears to be carried over into the crystalline form, the scratch hardness of which is certainly below that of steel, but which resists crushing to an extraordinary degree. The thermal properties of B_2O_3 have been studied in considerable detail in the form of glass by G. S. Parks, W. E. S. Turner and others, but the thermal properties of the crystals still remain to be investigated. The fact that both the melting point and the softening point are relatively low on the temperature scale makes it an ideal substance to be studied from this point of view. An X-ray study of the constitution of the glass has been made by B. E. Warren, and has led to conclusions which are in essential agreement with those arrived at by W. H. Zachariasen on more qualitative grounds. The X-ray study of the structure of the crystals has been begun.

In studying the solubilities, all the crystalline phases, except ice, have been observed to sink in the coexistent solutions; for these denser phases, the immediate effect of increasing pressures is to raise the melting temperatures. For B_2O_3 a very rough estimate of the rise is 3° per 100 atmospheres, made by neglecting the effect of compressibility, and by assuming (1) that the latent heat of melting is of the order above calculated, (2) that the thermal expansion of the crystals is about the same as that of the glass. For ice, the melting temperature is first lowered at the rate of 1° per 100 atmospheres increase of pressure, but beyond 2000 atmospheres, the melting temperature also begins to rise.

Many other problems could be discussed here. We shall confine ourselves to pointing out that the volatility relations in this system are of special interest, differing from those usually encountered in that both components are volatile within the system, although B_2O_3 itself is practically nonvolatile in the complete absence of water. Within the system, the B_2O_3 content of the vapor must be ascribed to the formation of compounds stable in the vapor phase. The system is not unique in this respect, but very little is known in the literature concerning such behavior.

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SUMMARY.

The equilibrium diagram for the system of water and boron oxide has been established by measuring the solubility over the whole range of compositions.

The crystalline phases which occur in the system are ice, H_3BO_3, three modifications of HBO_2, which are monotropically related to each other, and crystalline B_2O_3. Solubility relations have been determined for each of these phases.

The solubility curve for ice extends only from the melting point of ice to the cryohydric point at —0.76° C. The curve for H_3BO_3 rises smoothly from this point to a maximum at the melting point (metastable) of H_3BO_3, 170.9° C., and then descends to end at the metastable eutectic for HBO_2III and H_3BO_3.

The three forms of HBO_2 melt congruently, HBO_2I, the stable modification, at 236° C., and HBO_2II and HBO_2III, both metastable, at 200.9° C. and 176.0° C., respectively.

Their solubility curves have flat maxima at the composition HBO_2. The curve for the stable form, HBO_2I, intersects the curve for H_3BO_3 at 169° C., at which point H_3BO_3 decomposes to form HBO_2I and a solution of the equilibrium composition. The reaction is an abnormally sluggish one, so that the metastable continuation of the solubility curve of H_3BO_3 is realized as if HBO_2I did not exist. The curves for HBO_2II and HBO_2III intersect that of H_3BO_3 at metastable eutectics located at 169.6° C. and 158.5° C., in the order given.

Crystalline B_2O_3 melts at 450° ± 2° C. It has been crystallized from solution in sealed tubes, as well as in open vessels at atmospheric pressure, and various factors influencing its spontaneous growth have been established. The solubility curve for B_2O_3 extends from the melting point to the intersection with the curve of HBO_2I at 235° C., and with that of HBO_2II at 200° C. Both of these points are eutectics, the second being metastable.

P — T — X relations for the saturated solutions have been evaluated by combining the solubility data with deductions based on existing vapor pressure measurements. The resulting diagram, described in the text, brings out, among other things, the interesting fact that crystalline B_2O_3 can coexist with solutions at a vapor pressure of about 3 atmospheres in the neighborhood of 280° C. The oxide crystallizes relatively rapidly in sealed tubes in this region of temperature. The oxide crystallizes exceedingly slowly, on the other hand, from the nearly anhydrous melts of vitreous B_2O_3, and never spontaneously, in this region of composition. The spontaneous crystallization is initiated, in the more aqueous solutions, by the presence of HBO_2I, but not by the presence of the other modifications of metaboric acid.

The crystallographic and optical properties of the new crystal phases were measured, and are described in detail in the text.