Summary

It is shown that the integral heat of sorption of water vapor by massive gold is described by the equation $H = mW^n$, which is identical in form with the equation of Lamb and Coolidge for the sorption of organic vapors by charcoal.

The consequences of this observation are discussed and a possible mechanism by which the sorption occurs is considered.

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Hydrides of Boron. II. The Preparation of B_5H_{11}: Its Thermal Decomposition and Reaction with Hydrogen

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The development of a rapid and efficient method of preparing diborane (B_2H_6)[1] has made desirable the finding of efficient methods of preparing from it the less volatile hydrides of boron. Our experiments in this direction have led to the development of a satisfactory procedure for the preparation of the hydride B_5H_{11} and to a study of the properties of this hitherto little known substance. These investigations, in turn, have made possible improvements in the preparation of B_5H_9 from diborane, and have indicated a method by which useful quantities of the tetraborane (B_4H_{10}) may be prepared without recourse to the less efficient procedures involving the use of boron alloys.

When the pentaborane, B_5H_{11}, is heated at 100° without addition of excess of hydrogen, the first detectable effect is the production of small quantities of hydrogen, diborane, tetraborane and traces of a slightly volatile substance which seems to be an octaborane. Non-volatile solids appear soon afterward, but the formation of the latter seems to be inhibited to a certain extent by the accumulation of hydrogen. Within an hour the system, involving the substances named above, seems to reach a condition of equilibrium which is slowly shifted by the very gradual formation of B_5H_9,[2] traces of $B_{10}H_{14}$ and the non-volatile solids.

The indications that reversible changes are involved in these reactions led to the study of the effect of a high initial concentration of hydrogen. Under these conditions, the first reaction proceeds almost entirely according to the equation $2B_5H_{11} + 2H_2 \rightleftarrows 2B_4H_{10} + B_2H_6$. The tetraborane reacts further, but more slowly, mainly according to the equation B_4H_{10} +

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(1) Schlesinger and Burg, THIS JOURNAL, **53**, 4321 (1931).

(2) Because of the existence of the two substances B_5H_9 and B_5H_{11} which cannot be satisfactorily named till more is known about their structure, we shall refer to them only by formula. The term pentaborane will hereinafter be used only to refer to mixtures of the two.

$H_2 \rightleftarrows 2B_2H_6$, until the whole system reaches a state of equilibrium in which the concentrations of B_4H_{10} and B_5H_{11} are low. Here, also, further heating results in the formation of B_5H_9, $B_{10}H_{14}$ and the non-volatile solids; the last are formed much more slowly and are much lighter in color than those produced in the absence of hydrogen.[3]

Although the presence of hydrogen inhibits the formation of the non-volatile hydrides, the latter do not themselves react with hydrogen to reproduce the volatile substance. The effect of the hydrogen is, therefore, best explained by assuming that it decreases the concentration of slightly volatile products (among which may be the octaborane mentioned above) which yield the solids by a secondary reaction.

On the other hand, hydrogen seems not to interfere at all with the formation of $B_{10}H_{14}$ and B_5H_9. For this reason it has been found possible to improve the yields of the latter by adding a high concentration of hydrogen to the reaction mixture before heating it.

The thermal decomposition of B_5H_{11} and its reaction with hydrogen are most easily understood by supposing that the structure of this substance is an open chain, whose most probable mode of decomposition is a break at one end. This picture accounts very well for the reaction with hydrogen, which produces one molecule of tetraborane from each molecule of pentaborane used up. This reaction may be an addition of hydrogen to the tetraboryl and monoboryl radicals produced by the breakdown of the five-atomic chain. The same assumption would account for the formation of an octaborane in the absence of hydrogen, under which conditions some of the tetraboryl radicals might unite to form eight-atomic chains.

Whatever the mechanism, the reaction of B_5H_{11} with hydrogen gives us an efficient means of preparing tetraborane. The development of a convenient technique for carrying on this reaction on a large scale should make this substance considerably more easily available than it has been before. A flow method should be suitable for the purpose.

Stock and Siecke[4] have given reasons for believing in the existence of a third pentaborane, distinct from B_5H_9 and B_5H_{11}. We have been unable to find any evidence in support of this assumption. On the contrary, our observations of the behavior of B_5H_{11}, whether alone or mixed with a large proportion of B_5H_9, agree perfectly with the observations of Stock and Siecke on the behavior of "$B_5H_{>9}$" in its mixtures with B_5H_9. It is reasonable to believe that "$B_5H_{>9}$" and B_5H_{11} are identical. At the same time we must recognize that our observations on B_5H_{11} do not agree perfectly with those of Stock and Siecke, who were led to suppose that B_5H_{11} is an intermediate in the formation of $B_{10}H_{14}$. It seems best to ascribe the dis-

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(3) This effect of hydrogen makes it useful as a preservative of the volatile hydrides. A sample of diborane at room temperature produces non-volatile solids amounting to 10% of the sample in one year. In the presence of an equal volume of hydrogen, the loss of volatile substances is scarcely observable.

(4) Stock and Siecke, *Ber.*, **57B**, 562 (1924).

crepancies to differences in the quantities and kinds of impurities, rather than to any difference in the substance itself.

The Preparation of B_5H_{11}

I. At Room Temperature.—In our first experiments we obtained B_5H_{11} by allowing samples of diborane to stand for months at a time in sealed bulbs at room temperature (20–30°). The material in each bulb was introduced into the vacuum apparatus by means of the tube-opener[5] and the products were separated by the method of fractional condensation (B_5H_{11} trapped at $-85°$, B_4H_{10} at $-124°$ and B_2H_6 condensed at $-190°$). The results are shown in Table I.

TABLE I

Conditions			Products (cc. gas)			Results	
Vol. of B_2H_6, cc.	Vol. of bulb, cc.	Time, months	Hydrogen	B_4H_{10}	B_5H_{11}	% Reaction of B_2H_6	% Yield B_5H_{11} + B_4H_{10}, %
1050	3400	0.5	..	...	2.5	0.6	100
447	1050	3.3	37.6	1.4	8.3	8.5	80
495	600	3.3	37.0	1.4	8.3	7.7	80
380	1050	13.5	88.8	6.8	8.0	21.8	40
1080	1100	4.0	111.0	13.0	20.6	9.7	75

In each case except the first, the bulb had become iridescent, showing that non-volatile boron hydrides had been formed, and a few small volatile crystals, evidently $B_{10}H_{14}$, had appeared.

Comparison of these results shows that the ratio of B_5H_{11} to diborane tends toward an upper limit, reached in a time near three months, at which point the rate of removal of the B_5H_{11}[6] becomes equal to its rate of formation. The results indicate that the preparation of B_5H_{11} at a temperature near 25° can be made most efficient by allowing each sample to stand about six weeks at a time. The B_5H_{11} so obtained is less contaminated with B_5H_9 than that obtained after longer standing at room temperature.

II. The Flow Method.—The preceding method is too slow for the preparation of large quantities of B_5H_{11}. The rate of reaction is increased greatly by exposing the diborane to higher temperatures, which must be applied only for short periods of time in order to avoid decomposing the product. The reaction is carried out quickly and conveniently by the use of a flow method, employing the apparatus shown in Fig. 1.

In this apparatus M is a 15-cc. measuring tube having 10 mm. internal diameter and 1 mm. wall thickness. The U-tube U4A is made of tubing having 15 mm. internal diameter and is 15 mm. high; its volume is 55 cc.[7] C is a small in-sealed capillary tube which regulates the flow rate. The rate of flow may be changed by replacing one capil-

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(5) Stock, *Ber.*, **51**, 985 (1918).

(6) This removal may occur by decomposition to form non-volatile solids, or by reaction with hydrogen to give diborane and tetraborane.

(7) It should be mentioned that the U-tube used in our experiments happened to be etched in places (about one-fifth of the heated area). It is shown below that the formation of B_5H_{11} seems to be a wall-catalyzed reaction. The etching therefore may be a factor in determining the yield.

lary tube by another. The size of U4 is not critical, but it should be wide enough to allow condensation of the whole sample of diborane (one or two liters of gas) without stoppage. The system is connected through the mercury float-valve V 11 to the central tube of the apparatus.

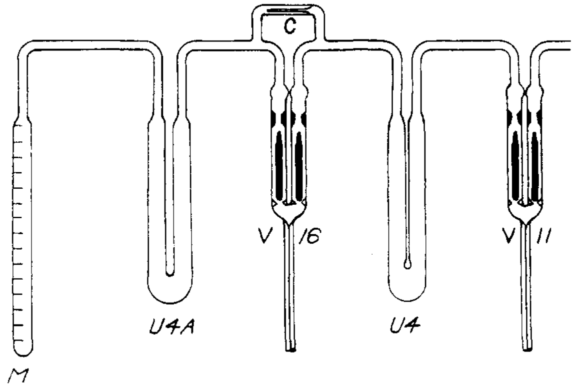

Fig. 1.

The diborane evaporates from M, which is held at a temperature of −78.5° (pressure near two atmospheres). It passes through U4A, which is kept at a suitable temperature (100 to 120°, depending on the experiment), and then goes with the reaction products through the capillary tube and is condensed in U4 at −196°. The hydrogen, which passes into the central tube, is pumped out by a Töpler pump and measured. Its quantity serves as an indication of the extent of reaction. The condensate in U4 may be returned to M and the process repeated again and again, to convert any desired fraction of the diborane into B_5H_{11} and B_4H_{10}. The results of these experiments are shown in Table II.

TABLE II

Conditions			Products, cc. of gas			Results		
Effective vol. of diborane, cc.	Flow rate, cc./min.	Temp. of U4A, °C.	H_2	B_4H_{10}	B_6H_{11}	B_2H_6 used up	% Reaction	Yield of B_5H_{11} + B_4H_{10}, %
1700	14	100	30.6	4.0	13.0	41	2.3	99
4620	14	100	84.0	10.4	36.2	114	2.5	99.5
6760	28	100	39.6	..	..	...	0.8	..
6640	28	110	111.0	..	..	...	2.1	..
11410	30	115	301.3	16.0	135.0	390	3.5	94.7

In this table the effective volume of diborane is the product of the average volume of the sample by the number of repetitions of the passage. The flow rate is the volume of gas (referred to standard conditions) passing through per minute. For the third and fourth of these experiments the percentage reaction was calculated by comparison with the quantities of hydrogen produced in the first two experiments. In the fourth experiment the temperature of U4A during the first five minutes was 120°. In that time 8 cc. of hydrogen was produced, and solid products appeared in the hot region. In the fifth experiment the temperature sometimes rose as high as 119° for short periods of time. It is believed that the main loss of material, due to the formation of solids, occurred during such intervals. There is good reason to believe that 115° is the temperature for greatest efficiency under the conditions here described.

Physical Constants.—The most trustworthy determinations of the vapor tensions and melting point of B_5H_{11} were made with a sample obtained from 1100 cc. of diborane which had stood six weeks in diffuse light at room temperature, in the presence of 300 cc. of hydrogen. The sample, 5.6 cc. of gas, was subjected to a long series of fractional condensations, by which 4.6 cc. of it was purified to the last possible degree. The vapor tensions of all fractions of this sample were exactly the same: 53.0 mm. at 0° (mercury at room temperature). The two determinations of the melting point of this sample gave the values −123.3° and −123.4° (measured by means of the ethylene vapor tension thermometer).

The vapor tensions were measured at different temperatures, established in a well-stirred ether bath and measured by means of a carefully calibrated alcohol thermometer (graduated to 0.2°). Each value given in Table III is the average of at least two measurements. The pressures were corrected to 0° by subtracting 0.45%.

TABLE III

t, °C.	−43.6	−39.0	−35.8	−33.4	−31.5	−25.5	−23.4	−20.2
p, mm.	3.5	5.0	6.1	7.2	8.5	12.2	14.0	17.0
t, °C.	−16.4	−13.4	−9.6	−7.0	−2.8	0.0	8.4	
p, mm.	21.7	25.6	32.1	35.8	45.6	52.8	77.7	

These values deviate less than 0.5° from the equation

$$\log_{10} p = 7.901 - (1690.3/T)$$

From this we calculate that the molal heat of vaporization is 7734 cal., and the normal boiling point, 63°. The Trouton constant is found to be 23.0 cal./deg. This abnormally high value suggests that any values taken at higher temperatures would have fallen below those predicted by the linear equation given above. The true boiling point might be one or two degrees higher than that given.

Results obtained with another sample illustrate the importance of selecting a sample as free as possible from B_5H_9. A 65-cc. sample (combined products of the second and third experiments of Table I and the first and second of Table II) was divided into eleven fractions; the middle seven showed vapor tensions varying 0.5 mm. from the average 54.5 mm., and melting points varying as much as 0.4° from the average value −123.2°. A 7.48-cc. portion of the sample, decomposed completely in a heated quartz tube, gave 5.49 volumes of hydrogen and a weight of boron corresponding to 4.86 volumes of gas. It is evident that such an analysis is not sensitive enough to detect the small quantity of B_5H_9 which seems to have been present.

The vapor tension values reported by Stock and Pohland[8] agree well with our values at low temperatures, but deviate markedly at higher temperatures (4 mm. high at 0°). It is evident that their sample was free from tetraborane, but must have been considerably contaminated with B_5H_9. This is to be expected in a sample accumulated in a period of ten months. One of our samples, obtained from diborane which had stood for thirteen and one-half months at room temperature, was analyzed by

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[8] Stock and Pohland, *Ber.*, **59B**, 2211 (1926).

complete thermal decomposition and found to contain about 12% B_5H_9. Its vapor tension at 0°, after the most rigorous fractionation, was 57 mm. The melting point was three degrees lower than that of our purest sample. The presence of B_5H_9 in carefully purified pentaborane samples is indicated very well by the deviation of the vapor pressure at 0° from the value 53.0 mm.

Heavier By-product of the Preparation.—The tenth fraction of the 65-cc. sample, 1.65 cc., had a vapor tension of 53 mm. at 0°, and the residue, 0.57 cc., only 23 mm. The latter was subjected to further fractionation, until a sample (0.25 cc.) having 10-mm. vapor pressure at 0° was obtained. The quantity was too small for positive identification, even by the very fine scale methods now available. Its volatility indicated a hexaborane; whether impure B_6H_{10} or an undiscovered hexaborane cannot be decided until a larger sample is available.

The Thermal Decomposition of B_5H_{11}

Preliminary Experiments.—A number of experiments, for the purpose of obtaining a qualitative idea of the behavior of B_5H_{11}, were performed. In most of these experiments the temperature was 100° and the container had a volume five or six times as great as the standard volume of the sample. It was learned that B_5H_{11} decomposes to give hydrogen, diborane, tetraborane, B_5H_9, $B_{10}H_{14}$ and a non-volatile yellow solid (evidently a mixture), easily hydrolyzable, but insoluble in any ordinary solvent. The yields of tetraborane and diborane were highest when the period of heating was short (ten minutes or less at 100°). The yields of B_5H_9 and $B_{10}H_{14}$ increased with the duration of heating. In most cases only unweighable traces of $B_{10}H_{14}$ were obtained. It was found, however, that reasonable yields of this substance were produced if one end of the tube remained at room temperature while the other end was heated. Neither B_5H_9 nor $B_{10}H_{14}$ appeared in detectable quantity before many other substances had been formed; in one experiment, for example, the sample was heated for twelve minutes at 100°, and was 75% decomposed to produce diborane, tetraborane and non-volatile solids. Only the minutest trace of $B_{10}H_{14}$ was produced, and the B_5H_9 was not detectable.

The non-volatile solid appeared only on the lower side of the container; it seemed to be formed by a homogeneous reaction, and then precipitated as a fine, gummy powder. Moreover, the formation of this substance could not be observed at all after the first hour at 100°, as shown by inverting the container at that time. This observation was explained by further experiments which showed that hydrogen inhibits the formation of the brown solids to a marked degree.

The Incipient Decomposition of B_5H_{11}.—It was observed in the preliminary experiments that a red-brown ring, appearing like the result of condensing a liquid which solidified afterward, always formed on the cool part of any of the tubes not completely immersed in the heating bath. This result made it seem worth while to search for a compound intermediate between B_5H_{11} and the brown solid which seemed to be one of its final decomposition products. In the first experiment in this direction, a 50.7-cc. sample of B_5H_{11} stood for seven and one-half hours at 25° (mainly in the liquid state), and 10% of it was decomposed to produce hydrogen, diborane, tetraborane, a trace of the brown solid, and a quantity of slightly volatile material too small for further study. In another experiment, 80.0 cc. of B_5H_{11} was held at 0° for eighty-eight hours, under conditions such that the reaction products more volatile than B_5H_{11} were removed as soon as they were formed. Five per cent. was decomposed, but the quantity of slightly volatile material again was too small to allow definite conclusions to be drawn.

Since these simple methods led to no clear-cut results, evidently because of the instability of the desired substance, we tried next a flow method. A 75-cc. sample of B_5H_{11} was placed in M (Fig. 1) and allowed to pass through U4A at 50°, under the pressure of its vapor at 22°. The rate of flow was such that the sample evaporated in thirty minutes. The flow was stopped twenty minutes later, and 0.2 cc. of hydrogen was pumped off. The products more volatile than B_5H_{11} (diborane and tetraborane) amounted to 0.4 cc. The remaining pentaborane was distilled very slowly through a U-tube immersed in a bath at $-60°$, and the fraction condensed at that temperature was found to consist of a very small quantity (estimated 0.1 to 0.2 cc. gas at standard conditions) of a substance having a vapor tension near 1 mm. at room temperature.

This process was repeated four times, with U4A at 65° (same sample of pentaborane); in each case the process was stopped as soon as the evaporation was complete. The reaction products were 2.5 cc. hydrogen, 3.75 cc. diborane, 1.00 cc. of tetraborane, and 0.5 cc. (gas) of a substance whose vapor tension at 24° was 1.2 mm. A small quantity of the brown non-volatile solid appeared in U4A. The slightly volatile substance was purified by the method of fractional condensation (trapped at $-33°$). Its uniformity was established by the fact that the vapor tension remained exactly the same while the volume of the apparatus was doubled and then tripled; about three quarters of the sample then was in the gas phase. The substance was found to be decidedly unstable: the vapor tension of a 0.15-cc. sample increased from 1.2 mm. to 1.7 mm. in five minutes at room temperature.

Evidence of the Existence of an Octaborane.—The most direct evidence for the belief that this substance is an octaborane is derived from the value of its vapor tension at 24°. The temperature at which each of the known hydrides of boron has a vapor tension of 1.2 mm. may be calculated from the vapor tension–temperature curves, and found to be as follows: B_2H_6, $-162°$; B_4H_{10}, $-90°$; B_5H_{11}, $-58°$;[9] B_6H_{10}, $-28°$;[10] $B_{10}H_{14}$, 63°. If we plot the temperature against the number of boron atoms in the molecule, we obtain a very regular curve whose intercept at 24° corresponds to 8.05 ± 0.10 boron atoms. It seems reasonably safe to conclude that the slightly volatile substance was an octaborane.

The Behavior of B_5H_{11} and B_4H_{10} with Hydrogen.—The details of the experiments on the behavior of B_5H_{11} with hydrogen are given in Table IV. In each experiment the sample was condensed in the bottom of the container (in most cases a bulb of the shape represented in Fig. 2); then pure hydrogen was added until the pressure was 750 mm., and the container was sealed off. On account of the low temperature of the lower end of the tube, the volume of the hydrogen (standard conditions) in most cases was 15–25% higher than the recorded volume of the bulb (fourth column). After immersion for a sharply controlled time in water at 100°, each bulb was cooled rapidly to room temperature and the contents at once introduced into the vacuum apparatus by means of the tube opener. In pumping the hydrogen out through a trap immersed in liquid nitrogen, it was not always possible to avoid some small loss of diborane. Each mixture of reaction products was separated completely into its components by the method of fractional condensation, and the volume of each component determined. The quantity of B_5H_9 in each of the pentaborane

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(9) Data for B_5H_9 below the melting point are not available.

(10) Estimated from the vapor tension at 0° (compared with B_5H_{11} by the use of Dühring's rule).

residues from experiments 2, 3 and 4 was determined by decomposing the measured sample in a hot quartz tube and measuring the volume of the hydrogen produced. These determinations were based on the reasonable assumption that the residues contained only B_5H_9 and B_5H_{11}.

In most of these experiments there was no observable formation of solids. Experiment 7 is exceptional, in that there was no hydrogen present at the start—brown solids therefore were formed. In each of Experiments 3c, 4b, and 4c, a barely observable scum of white non-volatile solid appeared.

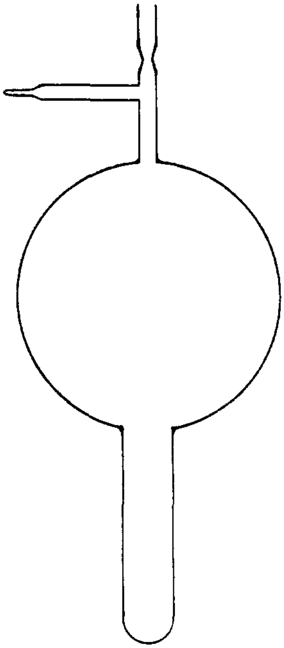

Fig. 2.

Attention is called to the fact that the term "pentaborane" used in the headings of several columns in Table IV refers to mixtures of B_5H_9 and B_5H_{11}. As has already been pointed out, it is exceedingly difficult to prepare samples of the latter entirely free from the former. For our present purpose a slight contamination is of no significance, provided due allowance is made for it in interpreting the results. Present analytical methods do not permit a determination of the amount of B_5H_9 in a sample of nearly pure B_5H_{11}. The data of column 10, "Percentage of pentaborane used up" therefore cannot be accurately transformed into "Percentage of B_5H_{11} used up" because we do not know precisely how pure the original samples in each experiment were. But we can show by the following analysis of the data that the error thus introduced cannot be large.

In Expts. 2 and 3, different portions of the same sample of "pentaborane" were heated at 100° for different periods. The product was then fractionated and the residual "pentaborane" was in each case reheated (2b, 3b). In Expt. 3 this procedure was repeated once more. Experiment 4 was similar, except that a different sample of "pentaborane" was used. As a result of the heating process, the percentage of B_5H_{11} in the residue was decreased to such an extent that a fairly reliable analysis of the percentage of B_5H_9 could be made. If we assume as a first approximation that none of the B_5H_9 thus found was a product of the reaction, *i. e.*, that all of it was present in the original samples, we should conclude that sample 2 originally contained 6.3%, sample 3, 5.3%, and sample 4, 3.2% B_5H_9. But these represent maximum values,[11] even though they represent relatively small contamination with B_5H_9. The difference in the percentage of B_5H_9 found for samples 2 and 3, on the assump-

(11) It has been shown by separate experiments that the treatment to which these samples was subjected does not appreciably affect B_5H_9. Of a sample of fairly pure B_5H_9, heated for five days at 125°, only 2% had undergone change.

TABLE IV

Conditions					Results						
1	2	3	4	5	6	7	8	9	10	11	12
Expt.	Vol. of penta-borane, cc.	Tension of penta-borane, at 0°, mm.	Vol. of container, cc.	Time of heating, min.	Vol. of residual penta-borane, cc.	Vol. of B_2H_6, cc.	Vol. of B_4H_{10}, cc.	Vol. of penta-borane used up, cc.	% Penta-borane used up	Tension penta-borane residue at 0° mm.	Final vol. of B_4H_9, cc.
1[a]	5.30	54.5	30	5	0.85	5.75	2.40	4.45	84	..	..
2a	22.2	54.4	370	10	5.90	10.7	14.8	16.3	74	56	..
2b	5.90	56	123	6	2.86	1.72	2.86	3.04	52	58	1.4
3a	42.2	54.5	565	4	24.5	9.05	17.0	17.7	58	55	..
3b	24.5	55	370	8	8.0	9.1	15.0	16.5	67	58	..
3c	8.00	58	123	20	2.66	6.2	2.64	5.34	67	63.5	2.25
4a	31.6	53.5	370	8	10.7	...	..	20.9	66	54.5	..
4b	10.7	55.0	123	20	2.80	...	..	7.90	74	56	..
4c[a]	2.80	56	30	25	1.85	...	..	0.95	34	61	1.0
5[b]	28.8	54.5	370	10	15.10	12.0	1.37	13.7	47	..	..
6	28.6	54.5	370	10	7.40	13.3	19.7	21.2	74	..	..
7[c]	27.5	54.5	358	10	6.90	15.2	18.0	20.6	75	..	..
8[d]	37.2	54.5	370	78 hrs.	35.35	1.60	1.50	1.85	5	..	..

[a] The container for this experiment was a cylindrical tube. Quantity of hydrogen, 60 cc. [b] No hydrogen present at the start. 8.35 cc. produced during the course of the experiment. [c] The container for this experiment was a series of bulbs, having an estimated ratio of wall area to volume 80% greater than that of the single large bulb used in experiment 6. [d] Entirely at room temperature.

tion that it was all present in the original sample, is too large to be explained by experimental error alone. It must, therefore, be due to the *formation* of more B_5H_9 during the reaction in Expt. 2 than during Expt. 3. This is just what would be expected, for in Expt. 2 the main portion of the material was heated a longer time than in Expt. 3. If this is true, then some of the B_5H_9 found in Expt. 4 must also have been a reaction product.

Hence we conclude that the samples used in Expts. 2 and 3 must have contained considerably less than 5% of B_5H_9 while the sample used in Expt. 4 must have contained less than 3% of B_5H_9. Not only are the total amounts of B_5H_9 relatively small in these samples, but the difference between the amount of contamination is small. Nevertheless, the sample used in Expts. 2 and 3 showed a vapor tension of 54.5 mm. at 0°, while the sample used in Expt. 4 showed 53.5 mm. The vapor tension at 0° thus is shown to be a very sensitive test of the degree of contamination. In the following, we shall consequently assume that two samples showing the same vapor tension, provided its value is not far from 53 mm., have the same composition.

Comparison of Expts. 2a, 3a, 4b, 6 and 7, all of which employed samples of pentaborane[12] having approximately the same vapor tension at 0°, shows that the initial reaction is fairly rapid, but that it soon becomes very slow. In four minutes (Expt. 3a), 58% of the pentaborane had been decomposed and in ten minutes about 75% (Expts. 2a, 6 and 7). Further heating, however, causes but little further change, for the percentage was

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(12) Experiments 1 and 5 are not included here because the conditions under which these were carried out were different from those of the others.

only slightly higher after twenty minutes of heating (Expt. 4b, in which the percentage reaction is slightly higher than the indicated 74%, because of higher B_5H_9 content). In Expt. 3a the amount of tetraborane formed differs by only 4% from the amount of B_5H_{11} used up, and the amount of diborane produced is slightly over one-half this quantity. These proportions agree reasonably well with the equation $2B_5H_{11} + 2H_2 \leftrightarrows 2B_4H_{10} + B_2H_6$. The deficiency of tetraborane and the excess of diborane are satisfactorily explained by a slower secondary reaction of the tetraborane to form diborane. In the other experiments under discussion, the discrepancies are larger, but always in the same direction; this is due to the fact that in these the time of heating is longer and the secondary reaction, therefore, has had time to proceed farther.

The situation was made clear by experiments in which tetraborane was heated with hydrogen. The tetraborane used for these experiments was obtained in very pure condition (vapor tension 388 mm. at 0°) by fractionating the products of the reaction of B_5H_{11} with hydrogen. The experiments, which are numbered as a continuation of Table IV, were as follows.

9. The bulb used in experiment 6 was filled with 14.1 cc. of tetraborane and somewhat more than one atmosphere pressure of pure hydrogen. During twenty minutes at 100°, 6.05 cc., or 43%, of the tetraborane was converted into 10.65 cc. of diborane and 0.45 cc. of B_5H_{11} (nearly pure).

10. The six-bulb container used in Expt. 7 was filled with 13.9 cc. of tetraborane and the usual excess of hydrogen. During twenty minutes at 100°, 7.40 cc., or 53%, of the tetraborane was converted into 12.30 cc. of diborane and 0.75 cc. of B_5H_{11} (vapor tension 54 mm. at 0°).

These results show that tetraborane reacts with hydrogen to form diborane, at a rate accounting very well for the deviations from the equation $2B_5H_{11} + 2H_2 \rightleftarrows 2B_4H_{10} + B_2H_6$. They also show that this reaction is reversible, a fact which may throw light on the sudden slowing of the reaction. But this reverse reaction is only a part of the reaction of tetraborane; it appears that most of it is converted into diborane. The final result must be an equilibrium[13] in which diborane is the predominating boron hydride. This statement is confirmed by the results of an experiment in which diborane and hydrogen were heated together for sixty-four hours at 100°. At the end of this time the 250-cc. bulb contained 150 cc. of hydrogen, 38 cc. of diborane, 0.5 cc. of B_4H_{10} and 2.2 cc. of pentaborane (nearly pure B_5H_9), along with some white solids.

The difference in the percentage reaction of tetraborane in Expts. 9 and 10 shows that the rate of reaction of tetraborane with hydrogen depends upon at least one wall-catalyzed process. It is especially evident that the rate of formation of B_5H_{11} is increased by increasing the wall area, for the

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[13] Even this equilibrium is slowly shifted by the irreversible formation of B_5H_9, $B_{11}H_{10}$ and nonvolatile solids. We may treat it as a true equilibrium because it can be established before any important quantities of these other substances are formed.

concentration of this substance at the end of each experiment was greater in number 10, which was carried out in a vessel of larger wall area.

Comparison of the behavior of B_5H_{11} with and without initial hydrogen at 100° (Expts. 5 and 6) shows that considerably more reaction occurs when hydrogen is present than when it is absent. This result is plausibly explained by supposing that the B_5H_{11} molecule first breaks up into radicals, which recombine to a large extent when hydrogen is absent. But a large excess of hydrogen prevents much of this recombination because these active radicals unite with it to form diborane and tetraborane, substances whose enduring qualities are greater than of B_5H_{11}; the reforming of B_5H_{11} is thus delayed. The alternate explanation, that hydrogen itself attacks the pentaborane chain, does not seem very probable.

In Expt. 8, which occurred at room temperature, it seems that the reaction of tetraborane with hydrogen occurred at a rate proportionally higher than in similar experiments at 100°; only 5% of the pentaborane was used up, yet the deficiency of tetraborane, below that required by the equation $2B_5H_{11} + 2H_2 = 2B_4H_{10} + B_2H_6$, was 19%. There might be many ways to account for this difference, but no uniquely satisfactory explanation appears.

The Preparation of B_5H_9.—We have performed a number of experiments in the direction of finding the most favorable conditions for the reaction by which diborane is converted into B_5H_9.[14] At the present writing the highest yield obtained represented only 33% of the volatile boron hydrides used up. It was found that a high concentration of hydrogen is an advantage, for it seems to interfere not at all with the rate of formation of B_5H_9, but hinders greatly the formation of non-volatile solids. Hydrogen chloride is not essential to the reaction, but it increases the yield. For this purpose, however, boron trichloride is quite as useful, and has the advantage that it does not convert boron hydride to boron chloride. The temperature used in most of the experiments was 120–130°; at 100° the yields were only about half as high, under comparable conditions. It was found most efficient to heat for three days at a time. The highest yield resulted when the diborane contained a fair quantity of tetraborane at the start; yet the use of a high concentration of tetraborane did not improve the yield, doubtless because of its comparatively rapid conversion to diborane under these conditions. Similar results were obtained when B_5H_{11} was heated for several days at 120°, with approximately one-third of its volume of boron trichloride and a large excess of hydrogen.

Much work is still to be done before we can be certain of the best conditions for the preparation of B_5H_9. This work is hindered by the lack of adequate working hypotheses concerning the mechanism of the reaction and the function of the boron chloride.

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(14) Schlesinger and Burg, THIS JOURNAL, **53**, 4331 (1931).

Summary

The preparation of B_5H_{11} in quantities suitable for experimental work has been accomplished by the use of a flow method involving diborane. Measurements upon a sample unusually free from B_5H_9 gave $-123.3°$ for the melting point and 53.0 mm. for the vapor tension at 0°.

The thermal decomposition of B_5H_{11} at first gives hydrogen, diborane, tetraborane and smaller quantities of a probable octaborane. Further heating produces non-volatile solids, B_5H_9 and $B_{10}H_{14}$. A ten-fold excess of hydrogen added at the start hinders so effectively the formation of substances less volatile than B_5H_{11} that it is possible to prepare diborane and tetraborane from B_5H_{11} practically without loss. The equilibrium system involving hydrogen, B_5H_{11}, tetraborane and diborane was studied to some extent at a temperature of 100°. Any one of these three boron hydrides may be prepared in quantity from one of the others, by a suitable adjustment of the experimental conditions. The preparation of useful quantities of tetraborane from diborane therefore is feasible.

Improvements in the method of preparing B_5H_9 by long heating of diborane have increased the yields to 33%.

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Hydrides of Boron. III. Dimethoxyborine

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Linkages between boron atoms seldom occur in compounds of boron with elements other than hydrogen. A striking contrast to this situation is presented by the boron hydrides, in all of which the boron atoms are linked together. The tendency for such linking is so strong that monoborine (BH_3) seems incapable of existence and the simplest hydride is diborane (B_2H_6), a circumstance not easily explained by any generally acceptable theory of valence. Substitution of halogens for hydrogen in diborane leads to compounds of the type B_2H_5X[1] and possibly $B_2H_4X_2$, but further substitution leads only to the boron trihalide. The only known simple derivative of monoborine, aside from those in which all of the hydrogen is replaced, is phenylborine ($C_6H_5BH_2$),[2] a compound which has been studied very little. It is thus of considerable interest to prepare compounds of the types HBR_2, H_2BR, HBX_2, and H_2BX, in the hope that a compound showing a tendency toward association by boron linkages may be obtained. Such work might lead to a better understanding of the factors which stabilize the boron to boron bond.

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(1) Stock, Kusz and Priesz, *Ber.*, **47**, 3115 (1914); Stock and Pohland, *ibid.*, **59B**, 2223 (1926).

(2) Pace, *Atti. accad. Lincei*, [VI] **10**, 195 (1929).