BOROHYDRATES.

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The following investigation arose out of an observation made while carrying out some preliminary experiments on the preparation of the hydrides of boron by the action of acids on magnesium boride. It was observed that the solutions obtained were strong reducing agents; and on treating the boride with water alone it, was found that the resulting solutions not only precipitated the heavy metals from the solutions of their salts, but on treatment with acids, effervesced, evolving quantities of a gas, which was found to be hydrogen. A preliminary investigation of the substances in the solutions was carried out by Dr. Travers and Mr. Hoy; and the results showed that there were present compounds of boron, oxygen, and hydrogen, to which the name 'borohydrates' was given. The results of these experiments were communicated to the Royal Society, under the title 'Borohydrates, Part I.' (Proc. Roy. Socy. *87*, 1912, p. 163). The paper also contained an account of the properties of the solutions, and of the methods employed in investigating them.

When Dr. Travers returned from leave in October 1912 the study of the solutions was taken up by himself and Mr. Gupta. It was then found that the solutions, which had previously been investigated, and which were already known to contain more than one substance in solution, had not been obtained in a condition such as was necessary for the accurate analysis of them. However, a very large number of experiments were carried out; a method for tho preparation of the boride was worked out, and tho reaction which took place when it was treated with water was studied. Finally the solutions themselves were carefully investigated, and most of the important problems connected with them were successfully solved.

2. *Magnesium boride.*

In the preliminary paper it was suggested that, as Winckler (Ber., *23* 772), and Moissan (C. r., *114*, 392) had indicated, there might exist borides of magnesium other than the compound Mg_3B_2, and that the borohydrates might be formed by the action of water upon one of them. After a number of experiments had been carried out with a view to determining whether the yield of the borohydrates could bo increased by varying the proportions in which the magnesium powder and boric acicl were pnwnt in the mixture from which the boride was prepared, and negative* results had been obtained, the study of magnesium boricle was taken up by one of us (11. C. K). The results of thaw, experiments, which will be published separately, tend to prove that then* in only one boride of magnesium, which has the formula AIg_3H_{tt} In practice we find that the hest method for preparing the boride for the purpose of these experiments is to heat a mixtuns of 1 .part of anhydrous boric acid and 2£ parts of magnesium powder in a covered crucible, through which a rapid current of dry hydrogen is passed, for 45 minutes to a red heat. It appears to be essential to the success of the experiment that the mixture should gently deflagrate about 5 minutes after the ban commenced; otherwise the reaction does not become complete, and the boride when treated with water gives a solution which contains a large quantity of magnesium metahorate.

3. *The, action of water on magnesium boride.*

The results of the experiments described in this seotion of the paper prove that magnesium horate is not a normal product of the action of water on magnesium boride, prepared in the manner described in the last section. On addition of water to **the** boride heat is evolved and gas is given off, rapidly at first, afterwards more slowly. In order to prevent the mixture from heating, we usually employed crushed ice instead of wafer, placed the flask containing the mixture in a bath of ice water. In certain experiments the hydrogen which given off was collected, and as the results of these experiments are of interest, those obtained in one case may be recorded.

Quantity of boride taken—80 grams.

Time in hours.	Volume of hydrogen in cubic centimetres afc 0° and 700, mm.
0	0
2	2,850
17	3,480
	5,100
65	7,920
89	10,400
113	32,080
137	1,3,080
189	16,000
258	15,260
303	15,850
418	10,600

When the rate of evolution of hydrogen fell to less than 100 ccs. in the 24 hours the experiment was brought to an end. The total quantity of gas evolved up to this point may "be expressed as 0.0187 grains of hydrogen per ^ram of the impure boride, and if the results of the experiment be plotted in the form of a curve, it will appear that this amount approaches the limiting value of the quantity of hydrogen which would be evolved on treating the boride with water for a very long time.

It aiay be observed here that during this experiment the water in contact with the boride was changed seven times, and the solutions so obtained were separately analysed. The results of the analyses will be given later in the paper (Table I p, 13.), bat it suffices for the present to state that the total boron removed as soluble borohydrate in the course of the experiment amounted to 0.6 grams. From observations of the rate of evolution of hydrogen, and the simultaneous formation of borohydrates, which have been recorded in the former paper, it appeared that the borohydrates were produced by the action of water on some boride other than Mg_3B_2. We have now, by means of numerous experiments, proved that this is not the case; for although water reacts, under the same conditions and with similar samples of boride, giving a fairly constant relationship between the hydrogen evolved and the hydroboron formed in solution, by varying the conditions, totally different results can be obtained. . It appears that the formation of the borohydrates is due to side reactions, the nature of "which have not yet been determined.

On analysis of a sample of the boride used in the experiment described above the following results were obtained :—

One grain of Loiide gave :—

Magnesium	...	...	...	0*6773 grams.
Boron	...	...	...	0'0718 „
Oxygen (diff.)		...	...	0'2300 „
Eesiciue (boron, insoluble in HC1)			...	Q'0209 „

The quantity of boron in 1 gram of the original mixture, calculated from the "boric oxide contained in it, vras 0"096 gram, though this figure is probably high, as the boric oxide was always slightly hydrated. The total boron in. 1 gram of the impure "boride obtained by heating the mixture was 0'093 gram. The free boron is derived from the magnesium boride, which., on heating, readily loses magnesium. The boride, as lias generally been assumed to be the case, is formed according to the equation:

$$6Mg + B,0_3 = 3MgO + Mg_3B,$$

The following experiment shows that the soluble boron is present practically entirely as the boricle, Mg_3B_2. *A* small quantity of the impure boride was dissolved in dilute hydrochloric acid in an exhausted flask, and the hydrogen, which was given off, was collected and measured. It was found that 1 gram of the impure boride gave off 0*0388 gram of hydrogen. Now 1 gram of the impure boride contains 0*0718 gram of boron, which is soluble in dilute hydrochloric acid, and if this is present as the boride Mg_3B_a, 1 gram of the impure boricle should according to the equation:

$$Mg_3B_2 + 6HC1 + 3\ H_20 = 3MgCl_3 + 2B\ (OH)_8 + 6H_2$$

evolve 0*0390 gram of hydrogen. Referring back to the experiment on the action of water on the impure boride, it will be seen that the limiting value of the quantity of hydrogen evolved from 1 gram is somewhat greater than 0*0187 gram or very nearly equal to 0*0195, that is to one-half of the quantity which satisfies the above equation. The reaction with water must, then, proceed according to the equation:

$$Mg_3B_2 + 6H_20 =\bullet \text{Mg»}B_t(OH)_a + 8\ H,$$

The main product being a magnesium derivative of a compound of the formula, $B(H_aO)_{n\ 5}$ which has not been isolated.

In order to confirm this result a quantity of the residue from action of water on the boride, an almost white powder, was taken and, after drying for a short time in vacuo, it was analysed. The following results were obtained :—

1 gram of the residue contained of boron soluble in dilute nitric acid,	0*0280	gram
1 gram of the residue gave of hydrogen with dilute hydrochloric acid.	0"0077	gram

Erom these results the ratio of the boron, expressed in gram atoms, the values for the hydrogen expressed in the same terms is 1: 3*03. Theoretically the ratio should be 1: 3, but as has been pointed out the reaction of the water with the boride was not quite complete.

So far as the present investigation goes, the importance of these experiments lies in the fact that they tend to prove that boric acid is not a product of the reaction of magnesium horide with water, and that this substance need not be considered as an impurity in the borohydrate solutions. It is interesting to note that if a solution of boric acid be added to the residue, a considerable quantity of the excess of magnesium oxide, \\hich is always present, passes into solution, but that little further action appears to take place. This reaction has not been investigated*

It is only necessary to add that not only does the compound $Mg_3B_2 (OH)_6$ appear to be inactive, so Jar as the evolution of the gas is concerned, but on treating it with hot cr cold water, no further quantity of soluble borohydrate is produced.

4. *MagneMum Meta-lorate.*

In the course of this research we have found it neces sary to investigate the properties of magnesium rnetahorate, but as the details of this investigation will form the subject of a separate paper by one of us (N. M. G.), the following brief statement of the facts will suffice for present purposes.

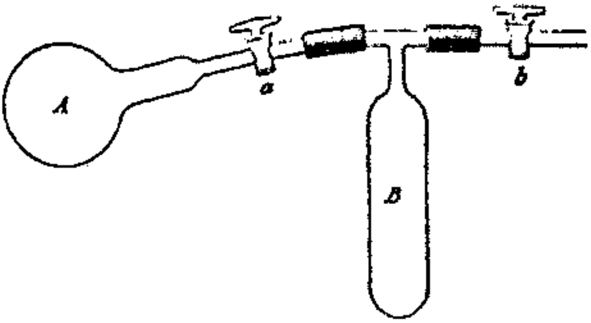
When a solution of boric acid is shaken for some time with * light′ magnesium oxide, a solution is formed which contains boric acid and magnesium oxide in proportions corresponding to the combination $Mg (B0_2)_2$. The solution is stable, but on standing deposits crystals of a slightly soluble metaborate. From the depression of the freezing point and the electrical conductivity it appears that the substance in solution is a strong electrolyte.

5. *Methods of analysis.*

As the solutions contained only magnesium and boron, in combination with hydrogen ond oxygen, the determination of these elements was a comparatively simple matter. The magnesium wits determined by taking 10 ccs. of the solution, evaporating to dryness with excess of hydrochloric acid and a little nitric acid, and after dissolving the residue in a little hydrochloric add, precipitating with ammonium phosphate -in presence of ammonia. It was found that it was not necessary to remove the boric acid from the solution. For the determination of the boric acid one of hvo methods was adopted. Either the solution was directly evaporated in a vacuum desiccator, over caustic soda, with about 3 ccs. of strong nitric acid, or the residue, obtained by the evaporation of the solution in vacuo, in the manner which will be described presently, was heated with 1 to 2 ccs. of strong nitric acid in a sealed bulb for some hours on a water bath, and the free nitric acid afterwards removed by evaporation in a desiccator. The residue, consisting of magnesium nitrate and free boric acid, was then washed into a crucible containing lime, which had been ignited to constant weight. The crucible was heated to 120° in an air-bath to drive off the water, and was then again ignited to constant weight. From the increase in weight of the crucible the quantity of magnesium oxide and boric acid, equivalent to the magnesium and boron present in the solution was directly determined; and knowing the quantity of magnesium which was present, the quantity of the boron was determined by difference.

As it was found that the solutions decomposed when heated, and absorbed oxygen when exposed to the air, the following method of evaporating them was adopted. A measured quantity, usually 5 or 10 ccs. of the solution was introduced into the bulb A (Plate I), to which in some cases a stopcock *a* was sealed. The bulb was connected with a vessel B, and through the stopcock *b* to an exhaust pump. The apparatus was exhausted, and while the bulb was immersed in a beaker of water at 30°, the vessel B was cooled with liquid air. Under these conditions it was possible to evaporate 10 ccs. of water in about two hours.

PLATE I.



The hydrogen evolved on addition of acid was determined by introducing a measured quantity of the liquid into a distillation flask of about 75 ccs. capacity, fitted with a tap funnel. The flask was connected with a Töpler pump, and after exhausting it, about 15 cc. of 30 per cent sulphuric acid was run into the flask. The hydrogen was then pumped off and measured. Before disconnecting the flask from the pump, 10 ccs. of N/10 iodine solution was added, and the small quantity of gas which was given off was also collected (p. 18). After disconnecting the flask a further quantity of iodine was, if necessary, added, and after standing for 24 hours in a dark cupboard, the excess of iodine was determined by means of sodium thiosulphate solution.

6. *Terminology.*

In this paper we shall refer to the quantity of hydrogen, expressed in gram equivalents, evolved on addition of acid to 100 ccs. of the solution as the Hydrogen Equivalent, and to the quantity of iodine, expressed in gram equivalents, absorbed by 100 ccs. of the acid solution as the Iodine Equivalent of the solution.

It will be convenient for the purpose of writing equations to denote the hydrogen which is evolved on addition of acid by H (Italic capital) and the hydrogen which is not so evolved by H (Roman capital). Thus we shall represent the substances which may exist in the solutions by the formulae:

$H_2\mathrm{H_4B_2O_2}$	α-hexahydro-dioxy-diboron
$H_4\mathrm{H_2B_2O_2}$	β-hexahydro-dioxy-diboron
$H_2\mathrm{H_4B_2O_2H_2,O}$	α-hexahydro-dioxy-diboron hydrate
$H_4\mathrm{H_2B_2O_2,H_2O}$	β-hexahydro-dioxy-diboron hydrate

The existence of the first of these compounds is doubtful, and at the best it must be considered to be an unstable substance, which changes readily into the second compound. The hydrates are weak acids, which are known in solution as the magnesium or ammonium salts.

7. *Classification of the solutions which are obtained by the action of water on magnesium boride.*

The solutions which we have examined fall into two classes. Those of Class A are obtained by treating one part of magnesium boride, prepared as described in Section 2 of this paper, with three parts of water, or of crushed ice and water, in an atmosphere of hydrogen, and keeping the mixture cool. It will be shown that these solutions are free from magnesium metaborate, and that the ratio of the value of the iodine equivalent to the sum of the values of the hydrogen and iodine equivalents, appears to lie between 0·5 and 0·44. Solutions of Class B are obtained by the action of water on samples of the boride which have not 'deflagrated' during the process of preparation, or by the action of water on a mixture of the boride, which has been properly prepared, with free boric acid. These solutions contain, as a rule, much magnesium metaborate, and the iodine equivalent is much higher than the hydrogen equivalent, the limiting value of the ratio of the equivalents being 2. The reaction between water and the boride is much more violent in the second case than in the first.

8. *Solution • of the First Class [A] which are free from magnesium nwta'borate.*

in the previous paper a number of samples of solutions of this class were studied, though more recent experiments have shown that, under the conditions under which they were prepared they probably contained impurities, and were somewhat decomposed. On evaporating the solutions in the cold, in vacuo, the distillate being collected in a receiver immersed in liquid air, no change appeared to take place, no hydrogen being evolved, till the last trace of liquid had evaporated. Hydrogen was then evolved rapidly ; but this change was not accompanied by loss of weight, beyond such as could be accounted for by measuring the hydrogen. On heating the residue a further quantity of hydrogen was evolved; but it appeared that the loss of weight which accompanied the change was equivalent to the weight of the gas. The experiments showed that after the last trace of water had disappeared from the distillation bulb, the residue did not lose water either on standing or on heating.

8a. *The nature of the residue obtained on evaporating the solutions.*

In the prelimnary paper on this subject (Borohydrates Part I), it was assumed that the residue obtained on. evaporating the solution in vacuo was boron trioxide. This assumption was based upon the fact that the residue absorbed little or no iodine, when allowed to stand for twenty-foujf hours in contact with that reagent in acid solution, and did not appear to react with oxidising agents. When the contents of the hulb in which the solution had been evaporated was washed out with dilute nitric acid, and the acid solution transferred to a platinum crucible containing lime for determining the boric acid present in it, it was found that the increase in weight of the crucible, after ignition, was almost exactly equal to the weight of the residue in the bulb.

It was assumed that the differnce between the boric acid in the residue, determined by this method, and the total boric acid in the original solution, could be accounted for by the fact that both the distillate obtained on evaporation, and the gas which was evolved during the process of distillation, contained boron. An experiment was carried out for the purpose of determining the total quantity of boron lost in this manner. Ten cubic centimetres of a solution, containing boron equivalent to 0*665 grams of B_aO_3 per 100 cc., was evaporated, and the distillate was collected in a receiver into which 2 cc. of strong nitric acid was introduced before immersing it in liquid air. The receiver was sealed while the contents were yet solid, and it was afterwards heated for some hours to 130°. The gas evolved on evaporating the solution and heating the residue was also collected and introduced into a tube containing 2 cc of strong nitric acid which was also sealed and heated. The boric acid in the two tubes was estimated in the usual manner. The following are the results of the experiment:—

Total boron as B_2O_3 in 100 cc. of solution	0*665	grain.
Boron in distillate	0'060	„
Boron in gas ... .., ...	0*049	„
Boron lost during evaporation ...	0*109	„

The loss is approximately 16 per cent. It was therefore necessary to investigate the residue itself.

It was found that when the nitric acid solution was allowed to evaporate *in vacuo* before determining the boric acid in it by the lime method, the increase in the weight of the lime exceeded the weight of the residue. "The results (Table 1) showed that the ratio of the weight of the residue, loss the weight of the magnesium oxide present in it, to the increase in weight of the lime, less the magnesium oxide, was as 1 : 1*25 to 1'30 and from this it appears that the boron in the residue is present as boron dioxide, B_2O_2-

In order to confirm this observation two quantities of ten cubic centimetres each of two solutions, were separately evaporated *in vacua*. The residue from one sample of each solution was washed out of the distillation bulb with dilute nitric acid, and the solution transferred to a platinum crucible containing lime. To the bulb containing the second samples of the solutions, two cubic centimetres of nitric acid was added, and the bulb was then sealed and heated on a water bath for a day. The bulb soon became filled .with red fumes, and it was evident that oxidation had taken place. The bulb was then cooled, and the contents washed with water into a crucible containing lime. The increase of weight of the crucible was determined in the usual manner. The following are the results of the experiments :—

Treatment with dilute nitric acid in the cold :—

	A.	B.
Weight of residue, less MgO ...	0.0214	0.0186
Increase in weight of lime, less MgO	0.0198	0.0188

After treatment with strong nitric acid in a sealed bulb :—

Weight of residue, less MgO	0.0197	0.0166
Increase in weight of lime, less MgO	0.0245	0.0216
Ratio	1.25	1.30

Numerous other determinations of the ratios of the weight of the residue and of the increase in the weight of the lime will be found elsewhere in the paper. (Table I).

It may be observed that the ratios between the molecular weights of boric anhydride, and other oxides of boron which might exist, are as follows :—

$$2B_2O_3/B_4O_5=1.129\ ;\ 2B_2O_3/B_4O_4=1.295\ ;$$
$$2B_2O_3/B_4O_3=1.520.$$

(*8b*). *Boron dioxide.*

We have not succeeded in isolating pure boron dioxide. When the original solution is evaporated to dryness and heated, a residue is left, which contains both B_2O_2 and MgO, and which, on standing in the cold for some hours with water, forms a clear solution. From this solution it appears to be impossible to precipitate the magnesia completely with ammonia. However the molecular weight of the boron compound can be determined in the solution which contains magnesium, on the supposition that the magnesium is present as a *borite*, which is practically completely dissociated. The calculation was made according to the following equation: —

$$\Delta=18.5\ \left(\frac{W}{M}+\frac{W'}{40}\right)$$

in which W is the weight of $(BO)_n$ per 100 ccs of the solution, and M its molecular weight, and W′ is the weight of MgO in the same volume of solution. The following are the results of the experiments :—

	A.	B.
Δ ...	0.223	0.150
W ...	0.486	0.356
W′ ...	0.122	0.0725
Ratio B_2O_2/MgO	2.95	3.64
M ...	54.8	57.1

The molecular weight of B_2O_2 calculated from the formula is 54. The magnesia content of one of the solutions was somewhat low, as some of the magnesia had not redissolved.

On heating the solution obtained by precipitating the magnesia from the original soultion with ammonia, a residue was obtained which consisted principally of B_2O_2, for on analysis it was found that the ratio of the weight of the residue to the weight of the B_2O_3 obtained from it was always about 1.3. However, the residue always contained traces of a substance which was insoluble in water, and in acids, and which appeared to be a lower oxide of boron, of the formula B_4O_3 (p. 35), and also traces of boric acid, which vitiated the values obtained for the molecular weights.

On evaporating the solution of B_2O_2 in air the oxide was converted into boric acid.

On allowing the solution to stand with excess of magnesium oxide in vacuo for some days, magnesium passed into solution, and it was found that the limiting quantity of magnesium which was taken up corresponded to a borite of the formula MgO, 2 B_2O_2. When ordinary light magnesia was used somewhat lower values were obtained, but when the magnesia was obtained by precipitating a solution of magnesium nitrate with ammonia, washing the precipitate with ammonia solution, and drying the precipitate in vacuo, the quantities of boron and magnesium in the solution corresponded to the above formula. The following is the result of the analysis of the solution :—

MgO in 5 ccs.	0.0231 gms. or 0.00058 gms, mols.
B_2O_2 in 5 ccs.	0.0611 „ or 0.00113 „ „
Ratio B_2O_2/MgO	1.94

Under the same conditions boric acid forms magnesium metaborate, MgO, B_2O_3.

When the ammoniacal solution of the oxide is evaporated in vacuo in the cold the residue is found to contain only a very small and variable quantity of ammonia,

(86'). *The results of analysis of solutions of the borohydrates which are free from magnesium metaborate.*

The solutions employed in these experiments were prepared in the manner described in § 3 of this paper, but the first extract obtained by allowing water (ice) to react with fresh boride was discarded, and most likely to contain impurities. The second and later extracts were taken for analysis, the first extracts being used for qualitative experiments, and for experiments in which it was not necessary to determine the boron content of the solutions. The errors in the previous work are due to the fact that we usually employed the first extracts.

The different samples of the boride used in the experiments were all prepared in the same manner, but were subjected to different treatment before adding water. The boride used in the first experiment, was treated first with methyl alcohol and was afterwards extracted with dry ether, which dissolves both boric acid and magnesium borate, for a day. Later, this process was abandoned as unnecessary.

TABLE I.

	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
H+1 ...	0·02135	0·0377	0·0382	0·02615	0·0175	0·02225	0·04135	0·538	0·0492	0·07825
MgO per 100ccs. solution	0·0565	0·097	0·0775	0·0495	0·0365	0·060	0·085	0·099	0·101	0·170
MgO in gram mols. ,,	0·0014	0·0024	0·0019	0·0012	0·0009	0·0015	0·0021	0·0025	0·0025	0·00425
Residue less MgO ,,	0·205	0·355	0·3115	0·2065	0·1535	0·1965	0·407	...	0·413	0·658
B_2O_3 ,,	0·265	...	0·3765	0·2625	0·1975	0·2445	...	0·5860	...	...
B in gram atoms ,,	0·00785	0·131	0·01075	0·0075	0·00565	0·0071	0·0151	0·0167	0·0164	0·0244
Ratio (H+I)/B ...	0·94	0·96	1·10	1·16	1·05	1·05	0·93	1·07	1·00	1·07
Ratio B/Mg ...	5·6	5·45	5·6	6·0	6·0	5·4	7·2	6·7	6·5	5·7
Ratio B_2O_3/Residue less MgO.	1·26	...	1·21	1·27	1·28	1·24	...	...	...	...

(8d) Discussion of the results of the analyses.

The results of these experiments show that, considering the unstable character of the substances in the solutions, a fairly close relationship exists betwen *the sum of the hydrogen and iodine equivalents*, and the quantities of boron, hydrogen, oxygen, and magnesium, which are present in combination. This relationship may be expressed by the emirical formula,

$$H_{18}B_6O_6, MgO.$$

The irregularity of the ratio (Boron)/(Magnesium) may be due to the fact that the boron was determined in the residues after the evaporation of the solutions, and it has been shown that in the process of evaporation a small quantity of boron passes over into the distillate. Though this boron is no doubt mainly derived from volatile hydroborons, which were originally present in the solutions, part of it may be derived from the decomposition of the borohydrates in the manner suggested on page 35. It may also be due to causes which are discussed in Section 8j. However, the results are sufficiently in agreement to make it probable that the formula set down above represents the actual composition of the substances in the solutions; and, since the compounds do not appear to lose water after evaporation of the solutions, the formula represents the composition of the residue at the moment at which the last trace of liquid has disappeared from the distillation flask. Analyses of the solutions obtained by precipitation of the magnesium by ammonia (p. 16) confirm this result. The relative values of the hydrogen and iodine equivalents will be discussed in Section 8j of the paper.

(8e) The mean molecular weight of the substances in the solutions.

Some preliminary experiments on the freezing points of the original solutions showed that the results might be vitiated by the presence of traces of volatile impurities; the following procedure was therefore adopted. A measured quantity of the solution was evaporated almost to dryness at the air temperature in a flask connected with a receiver immersed in liquid air. A measured quantity of water was then introduced into the flask, and the freezing point of the solution was measured and compared with the freezing point of pure water. In the following table the weights of the $(H_3BO)_n$ and MgO in 100 ccs. of the solutions are calculated from the sum of the hydrogen and iodine equivalents :—

$H+I$ ...	0·02155	0·02225	0·01625
$(H_3BO)_n$ in original solution	0·2155	0·2225	0·1625
MgO ,,	0·0497	0·0494	0·0361
$(H_3BO)_n$ in solution used	0·2155	0·1480	0·1080
MgO ,,	00497	0·0329	0-0240
Depression of freezing point	0·090°	0·065°	0·045°

The molecular weights (mean) of the residue $(H_3BO)_n$ can be calculated by means of the formula given on page 10, on the assumption that the magnesium is present as the salt of a weak acid, a hydrate of $(H_3BO)_n$, which is completely dissociated in solution. The values obtained in the three experiments are 58.7, 55.0, and 58.1. The value of *n* must therefore be 2, and the mean composition of the residue may be expressed by the formula $H_6B_2O_2$, for which the calculated molecular weight is 60.

(*8f*) *Are the solutions free from magnesium metaborate?*

It may be suggested that the magnesium is present in the solutions partly or wholly, though the latter alternative is altogether improbable, as magnesium metaborate, and it is not altogether easy to give a definite proof that magnesium metaborate is entirely absent. The most definite evidence on this point may be deduced from the difference between the behaviour of the borohydrate solutions, and solutions containing magnesium metaborate, when they are evaporated at the air temperature. Under these conditions the borohydrate solutions deposit no solid till the last traces of liquid are on the point of disappearing, the borohydrates being very soluble in water, and the residue contains no water. Solutions of magnesium metaborate, when they are evaporated in the same manner, throw out films of solid, and ultimately form a gelatinous mass, from which it is only possible to remove the water by heating strongly.

Finally the composition, and general behaviour of the borohydrates in the solutions make it improbable that magnesium metaborate is present.

(*8g*) *The replacement of magnesium by ammonium.*

When ammonia is added to the solutions, the magnesium is completely precipitated as magnesium hydroxide, the whole of the boron remaining in solution, and no gas is evolved. If the solution is then evaporated at the air temperature, either in a vacuum desiccator, or in a bulb connected with a receiver immersed in liquid air, till only a small quantity of liquid remains, it is found that the ammonia in the residue is approximately equivalent to the magnesium which was present in the original solution. It is impossible to obtain very exact results for such experiments ; for either the free ammonia may not be completely expelled from the liquid, or if the evaporation is carried too far, loss of ammonia will result from the hydrolysis of the ammonia salt in the solution. If the solution is evaporated to dryness a considerable proportion of the combined ammonia is lost. The following are the results of the experiments :—

Hydrogen equivalent + iodine equivalent	...	0·0356	
Ammonia in equivalents per 100 ccs.	...	0·00375	0·00460
$/NH_3$ ...	...	9·5	10·5

When the solution is evaporated completely to dryness and the residue is heated, a yellowish which appears to be mainly, boron dioxide, B_2O_2. It will be remembered that when the solution which contains magnesium is evaporated to dryness, the residue contains no water, and on heating only hydrogen gas is given off. The residue from the solution containing ammonia, however, contains ammonia and water in combination with the boron, and it appears that when the is small quantities of the boron oxide are liable to be carried with the vapours. This loss of boron be avoided by the cock on the distillation bulb closed while the bulb is heated, and only opening it at the end of the operation. following are the results of some of the experiments :—

Hydrogen equivalent + iodine equivalent			0·1018	0·0558	0·0394	
Residue from 100 ccs. of solution		...	0·881	0·488	0·379	0.252
B_2O_3 from residue	...	...	0114	...	0·485	0.334
Boron in gram atoms	...	...	0·0318	0·0181	0·139	
(H + I)/3B	...	...	1·09	1·03	0·94	

These results taken with the results of the analyses of the solutions containing magnesium, tend to prove that the solutions from which the magnesium has been precipitated by of ammonia contain boron, hydrogen, oxygen and the elements of ammonia and water, combined in the proportions $H_{18}B_6O_6$, $(NH_4)_2O$, but that hydrolysis and loss of ammonia on evaporation.

(8*h*) *The mean molecular weight of the substances present in the ammoniacal solution.*

As in the experiments with the original solutions, a quantity of the solution from which the magnesium had been precipitated by the addition of ammonia, and containing a known quantity of the borohydrates, calculated as $(H_3BO)_n$, was evaporated nearly to dryness at the air temperature, and redissolved in a known quantity of water. The freezing point of the solution was thea determined and compared with the freezing point of pure water. The following are the results of the experiments :—

$(H_3BO)_n$ in 100 ccs. solution		Depression of the freezing point	Molecular weight
0·247	...	0·110	41·8
0·248	...	0·110	41-9
0·139	...	0·070	36-9
0·214	...	0·105	37·9
0·622	...	0-280	41·3
0·186	...	0·085	40·5

The value obtained can be accounted for on the assumption that the ammonium salt which is present in the solution is almost completely dissociated. The solution may then be supposed to contain :—

$$2\ H_6B_2O_2 \quad + \quad \overset{+\ +}{H_6B_2O_2} \quad + \quad 2\ NH_4$$

The mean molecular weight should then be $(60 \times 3/5)$ or 36, which is very close to the value actually obtained. The molecular weight of the medium $(H_3\ BO)_n$ might equally well be calculated by means of the equation used in Section 8e.

The changes in the relative values of the hydrogen and iodine equivalents which take place on adding ammonia to the solutions will be dealt with in section (8j) of this paper.

8*i*. *The physical and chemical properties of the solutions.*

As the solutions decompose slowly at the ordinary temperatures, evolving bubbles of hydrogen, and effervesce in the presence of such substances as platinum black, it has been impossible to determine their electrical conductivities, and similar properties. They are usually, but not always, yellow in colour, the colour being apparently due to the presence of colloidal boron. Their behaviour towards acids, and ammonia has already been described. They precipitate silver and mercury from their solutions immediately. With solutions of copper salts the nature of the reaction appears to depend upon the relative concentrations of the solutions, either a black precipitate of amorphous boron is formed, or a yellowish rod substance, which is apparently copper hydride, is thrown down. On addition of a neutral solution of lead acetate a grey precipitate is thrown down, and though this appears to contain some metallic lead, it consists mainly of the lead salts of the borohydrates; and since if sufficient of the reagent is added almost the whole of the boron is removed from the solution, it appears that both the compounds $H_6B_2O_2$ and $H_6B_2O_2, H_2O$ can form insoluble lead derivatives. An attempt was made to make use of this reaction to separate the two borohydrates which are present in the solutions which are free from magnesium borate, but it was not successful. Some experiments were carried out by Mr. Pal. M. Sc., in this laboratory to determine whether the borohydrates entered into combination with organic aldehydes. The experiments were unsuccessful, and it was found in the case of benzaldehyde that the only product was benzyl alcohol.

8j. The relationship between the hydrogen and iodine equivalents.

It must first be pointed out that it is impossible to determine the values of these constants for the solutions with a degree of accuracy greater than two or three per cent, and that such differences are some times observed between the results of experiments carried out with the same solutions, and apparently tinder the same conditions. Further, when, after adding of acid to the solution, iodine solution is added, a small quantity of hydrogen is always evolved. The quantity of hydrogen varies considerably, as the results of the experiments show, the quantity of hydrogen being expressed in gram atoms of hydrogen per 100 ccs. of solution.

Value of (H + I)	Gas.
0·0613	0·0017
0'0686	0·0018
0·0347	0·0011

The quantity of gas given off is usually 2 to 8 per cent of the sum of the hydrogen and iodine equivalents.

The question to be decided is, should the correction be applied to the hydrogen or to the iodine equivalent, and as we have no positive evidence to guide us in either direction we have, unless it has been expressly stated to the contrary, added the hydrogen evolved on adding iodine to the hydrogen evolved on adding acid to the original solution. Thus, the values of the hydrogen equivalents are possibly somewhat too high, and the values of the hydrogen equivalents too low by a corresponding amount.

On the other hand it must be borne in mind that on evaporation of the solutions the distillate is always found to contain some volatile compounds containing boron. These compounds are oxidised by iodine solution, and the presence of them in the original solutions would probably tend to raise the values of the iodine equivalents.

When the solutions were allowed to stand it was observed that, if air was not present, the values of the hydrogen and iodine equivalents usually decreased slowly, hydrogen being given off, but that if air had access to the solutions, the iodine equivalent decreased rapidly. The fact was confirmed by means of several experiments, of which the following is an example. The time is expressed in days :—

	Liquid in sealed tubes.			Liquid in flask exposed to the air.	
Time.	• II.	I	Gas.	II.	I.
0	0·0288	00225	0 0000	0·0288	0·0225
1	0·02555	0·0220	0·0048	0·0266	0·0174
4	0·02535	0 0210	0·0058	0·02765	0·0134
7	0·02525	0·0203	0*00845	0·0269	00131
13	...	...	...	00270	00123

The fact that the hydrogen equivalent in the sealed tube experiment decreased more rapidly than in the flask experiment appears to be due to the fact that the evolution of gas, which is consequent on the fall in the value of the hydrogen equivalent, is much influenced by contact catalysis. It was found that, in making comparative experiments on the rate of decomposition of the solutions, it was important that the vessels containing the solutions, should be of the same kind of glass, and that they should have been treated in the same manner. New glass appeared to have marked action in decomposing the solutions. It was also found that samples of the solutions which were very yellow, and which therefore contained much colloidal boron, decomposed very rapidly.

In view of these facts, in our later experiments particular precautions were taken to exclude air during the preparation of the borohydrate solutions, and by using ice, instead of water, to prevent the mixture becoming hot. In spite of these precautions, we found considerable differences between the ratio of the values of the hydrogen and iodine equivalents for different solutions, as is shown by the figures in Table II, in which we have set down the constants for the last tweny-four solutions which were examined, and the values of the ratio I/(H + I). The figures in the column *a* indicate whether the solution was the product of the first or subsequent extractions of the boride with water.

TABLE II.

No.	a.	H	I	H+I	I/(H+I)
1.	(1).	0·0231	0·0252	0·0483	0·52
2	(3)	0·01615	0·0152	0·03135	0·48
3	(1)	0·0719	0·0682	0·141	0·49
4	(2)	0·03305	0·0228	0·05585	0·41
5	(1)	0·0308	0·02855	0·05935	0·48
6	(2)	0·0232	0·0188	0·0420	0·45
7	(3)	0·0354	0·0346	0·0700	0·49
8	(1)	0·0410	0·0368	0·0778	0·47
9	(1)	0·0804	0·0540	0·1345	0·41
10	(2)	0·0466	0·0452	0·0918	0·49
11	(3)	0·0419	0·03645	0·07835	0·46
12	(1)	0·0320	0·0145	0·0565	0·43
13	(2)	0·01255	0·0800	0·02055	0·39
14	(2)	0·0355	0·0258	0·0613	0·42
15	(2)	0·0195	0·0179	0·0374	0·48
16	(1)	0·0305	0·0268	0·0573	0·47
17	(2)	0·0288	0·0225	0·0513	0·43
18	(1)	0·04325	0·0320	0·07525	0·43
19	(1)	0·0410	0·0368	0·0778	0·47
20	(1)	0·0804	0·0541	0·1345	0·40
21	(2)	0·0466	0·0452	0·0918	0·49
22	(3)	0·0419	0·03645	0·07935	0·47
23	(4)	0·0290	0·0202	0·0492	0·41
24	(1)	0·0719	0·0682	0·1401	0·49

Now if the solutions contain compounds of the formula H_6-X, which may be written H_4H_2-X or H_2H_4-X, according as four or two atoms of hydrogen are eliminated by the action of acid, the proportion in which they are present can be determined from the value of the ratio I(H+I). Thus:

Proportions in which the compounds are present.	value of Ratio I/(H + I)
a. Only $H_4\mathrm{H}_2$-X	0·33
b. 2/3 $H_4\mathrm{H}_2$-X — 1/3 $H_2\mathrm{H}_4$-X	0·44
c. $H_4\mathrm{H}_2$-X — $H_2\mathrm{H}_4$-X	0·50
d. Only $H_2\mathrm{H}_4$-X	0.66

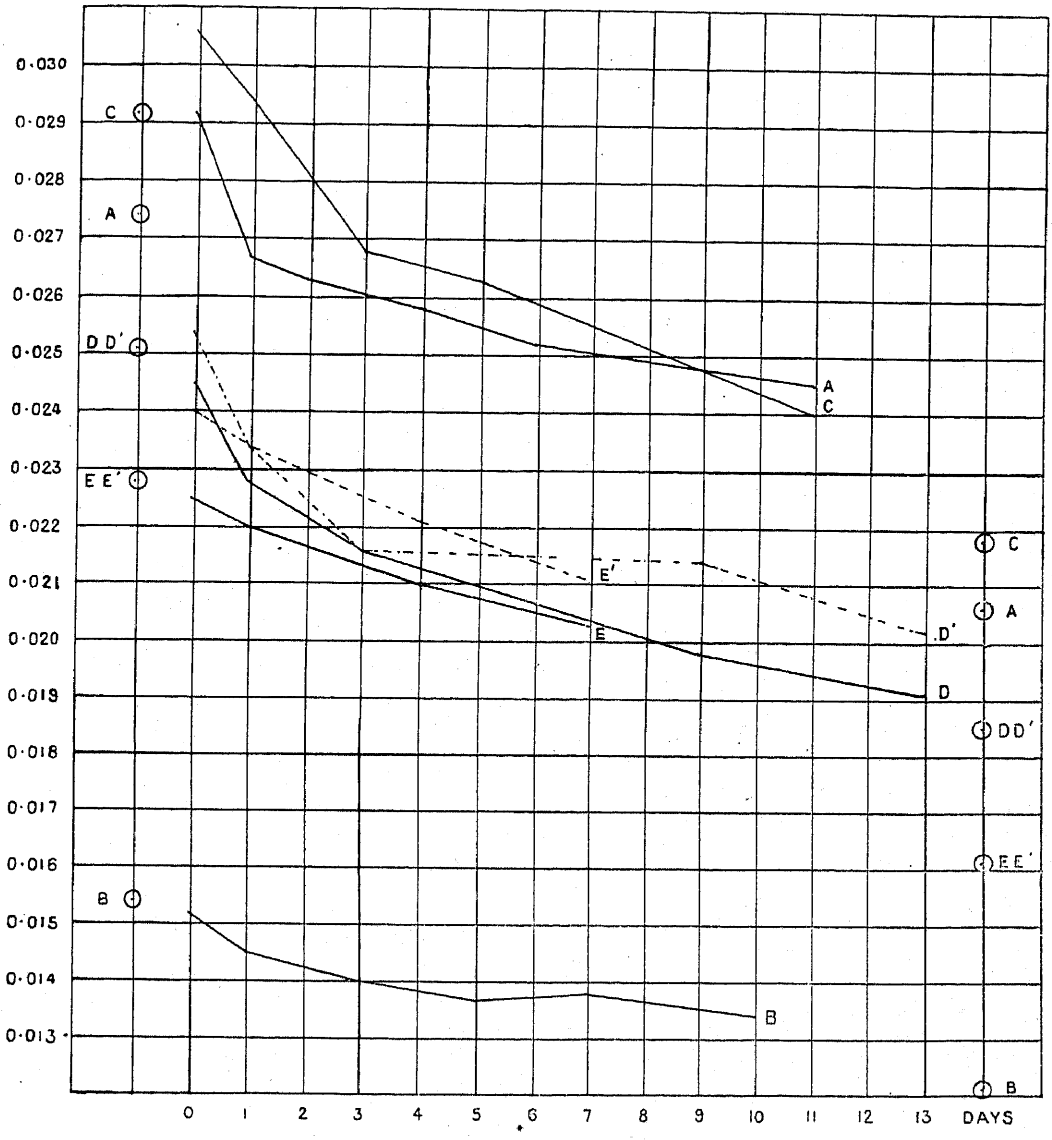
From the figures set down in Table II, it is impossible to arrive at a definite decision as to whether the normal composition of the mixture is represented by *b* or *c*. With a view to throwing light on the subject we carried out a series of experiments on the decomposition of the solution in sealed tubes. Quantities of 5 ccs. of the solutions were introduced into glass tubes which were exhausted and sealed in such a manner that the gas evolved from the liquid could be pumped off and measured, and the hydrogen and iodine equivalents of the solutions afterwards determined. The solutions were kept at 25° during the experiments. A very large number of experiments were carried out, and the results of a selection of them, for which the value of (H+I) ranges from 0·0617 to 0·0379 are set down in Tables III. In Plate I the values of the iodine equivalents (ordinates) are plotted against the duration of the experiments in days. The points marked on the left hand side of the plate within circles are the values of 4/9(H+I), and those on the right hand side of the plate are the values of 1/3(H + I). In the experiments A, B, C, D, and E, the value of the hydrogen equivalent includes the value of the hydrogen evolved on adding iodine; in D′, and E′ this correction is applied to the iodine equivalent.

TABLE III.

	A.			*B.*			*C.*			*D.*		
Mean value H + I	0·0617			0·0384			0·0654			0·0565		
1/2 (H + I)	0·0308			0·0192			0·0327			0·0282		
4/9 (H + I)	0·0274			0·0162			0·0291			0·0251		
1/3 (H + I)	0·0206			0·0121			0·0218			0·01885		
Days.	Gas.	H.	I.	Gas.	H.	I.	Gas.	H.	I	Gas.	H.	I.
0	0·0	0·0344	0·02915	0·0	0·02015	0·01515	0·0	0·0352	0·0306	0·0	0·0320	0·0245
1	0·0033	...	0·0267	0·00235	0·0197	0·0145	0·00295	0·03325	0·0294	0·0055	0·0280	0·0228
2	0·00355	0·03185	0·0263	...	...	...	...	...	...	...	...	...
3	...	...	...	0·0034	0·0195	0·0140	0·0053	0·03275	0·0268	0·00785	0·0270	0·0216
4	0·0062	0·0298	0·0258	...	...	...	...	...	...	...	...	...
5	...	...	...	0·0040	0·01875	0·0137	0·0060	0·0331	0·0263	...	...	...
6	0·0074	0·0299	0·0252	...	...	...	...	...	...	...	...	...
7	...	...	...	0·00485	0·01860	0·0138	...	...	...	...	...	...
8	0·0082	0·0296	0·0250	...	...	...	0·0070	...	...	...	...	...
9	...	...	...	...	...	...	...	...	...	0·0122	...	0·0198
10	...	...	...	0·00545	0·01850	0·0134	...	...	...	...	...	...
11	0·0092	0·0280	0·0245	...	...	...	0·0103	0·0291	0·0240	...	...	...
12	...	...	...	...	...	...	...	...	...	...	...	...
13	...	...	...	...	...	...	...	...	...	0·01105	0·02785	0·0191

	D′			*E.*			*E′*		
Mean value H + I	0·0565			0·0513			0·0513		
1/2 (H + I)	0·0282			0·0256			0·0256		
4/9 (H + I)	0·0251			0·0228			0·0228		
1/3 (H + I)	0·01885			0·0171			0·0171		
Days.	Gas.	H.	I.	Gas.	H.	I.	Gas.	H.	I.
0	0·0	0·0311	0·0254	0·0	0·0288	0·0225	0·0	0·0273	0·0240
1	0·0055	0·0274	0·0234	0·0048	0·02555	0·0220	0·0048	0·0242	0·02335
2	...	...	...	...	...	...	...	...	...
3	0·00785	0·0264	0·0222	...	...	...	...	...	...
4	...	...	...	0·0058	0·02535	0·0210	0·0058	0·0243	0·02205
5	...	...	...	...	...	...	...	...	...
6	...	...	...	...	...	...	...	...	...
7	...	...	...	0·00645	0·02525	0·02035	0·0645	0·02445	0·0211
8	...	...	...						
9	0·0122	...	0·0214						
10	...	...	...						
11	...	...	...						
12	...	...	...						
13	0·01105	0.0268	0·02015						

PLATE II.


0·030
0·029
0·028
0·027
0·026
0·025
0·024
0·023
0·022
0·021
0·020
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0·018
0·017
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C
A
D D'
E E'
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13
DAYS

The changes which take place in the solutions are probably complex, for, besides the evolution of hydrogen which may accompany the change in the hydrogen or iodine equivalent, or both, a change may take place which may be represented by the equation:

$$H_2\mathrm{H}_4\text{-X} \quad = \quad H_4\mathrm{H}_2\text{-X};$$

and that such a change can take place is proved by the experiments on the action of ammonia on the solutions, which are described later in this section of the paper. If we consider the change in the iodine equivalent alone there may be some reason for supposing that such a change does takes place; on the other hand, the fact that the ratios of the hydrogen and iodine equivalents remains fairly constant during the experiments is opposed to any such conclusion. Thus:—

TABLE IV.

Time.		Values of ratio I/(H+I)						
		A.	B.	C.	D.	D'	E.	E'
0	days.	0·46	0·43	0·46	0·43	0·45	0.44	0.47
1	„	...	...	0·46	0·45	0·46		0·46
2	„	0·44	0·42	...	...	...		...
3	„	...	...	0·45	0·44	0.46	...	...
4	„	0·46	0·42	...	...	...	0·45	0·47
5	„	...	...	0·44	...	...	...	...
6	„	0·45	0·42	...	...	...	...	...
7	„	...	...	...	...	...	0·44	0·46
8	„	0·46	0·42	...	...	...	...	...
11	„	0·47	...	0·45	...	...	...	...

That the normal value of the ratio I/ (H + I) is 1/2 and that the solutions, when entirely undecomposed, contain compounds of the formulae $H_4\mathrm{H}_2$-X and $H_2\mathrm{H}_4$-X in equi-molecular proportions is the simplest explanation which can be attached to the results of these experiments, and of those set down in Table II. If however we accept it, we find some difficulty in reconciling them with the results of the analyses, and with the molecular weight determinations. Our experiments in this direction point to the conclusion that the original solutions contain *two molecules of a compound of the formula* $H_6B_2O_2$ *to one* molecule of a compound $H_6B_2O_3$, MgO. It is unlikely that the magnesium compound is merely a derivative of a simple hydrate of the former compound, and, as is shown in Section 9 of this paper, it probably has the formula $H_2\mathrm{H}_4\mathrm{B}_2\mathrm{O}_2$, MgO. The compound $\mathrm{H}_6\mathrm{B}_2\mathrm{O}_2$, which is present in the original solution must, then, have the formula $H_4\mathrm{H}_2\mathrm{B}_2\mathrm{O}_2$. However, the value of the ratio I/ (H + I) for such a mixture would be 4/9 (0·444); and though the experimental values of the ratios often appear to have this value, or to approach to it, they are more often either above or below it. That the value can be lower is explained by the experiments at the end of this Section of the paper, which prove that the α-hydrate $H_2\mathrm{H}_4\mathrm{B}_2\mathrm{O}_2$, $\mathrm{H}_2\mathrm{O}$ can change into a β-hydrate $H_4\mathrm{H}_2\mathrm{B}_2\mathrm{O}_2$, $\mathrm{H}_2\mathrm{O}$. That the value can be greater than 4/9 may be due either to the fact that the compound $H_2\mathrm{H}_4\mathrm{B}_2\mathrm{O}_2$, MgO is partly hydrolised in solution, some of the free hydrate being usually present in it, or that the compound $\mathrm{H}_6\mathrm{B}_2\mathrm{O}_2$ exists in the solutions mainly as $H_4\mathrm{H}_2\mathrm{B}_2\mathrm{O}_2$, but also to a small extent as an isomer $H_2\mathrm{H}_4\mathrm{B}_2\mathrm{O}_2$, which, being the less stable modification, changes readily into the more stable form. It would have been interesting to have obtained a complete solution of this part of the problem, but it does not appear possible to do so. However, the results of our experiments leave no room for doubt that the original solutions contain at least two substances, the compound $H_4\mathrm{H}_2\mathrm{B}_2\mathrm{O}_2$, which we shall call the β-hexahydro-dioxy-diboron, as the α-compound may also exist, and the compound $H_2\mathrm{H}_4\mathrm{B}_2\mathrm{O}_2$, MgO, the α-hexahydro-dioxy-diboron hydrate, which, as we shall now proceed to show, can be changed into the β-hydrate by the action of ammonia.

The action of ammonia on the solutions in sealed glass tubes was studied, and the results of the experiments are set down in Table V. The solutions employed were identical with those which were used in the experiments last described.

TABLE V.

Mean value of H+I for original solution.	0·0617	...	0·0364
1/3 (H+I) ...	0·0206	...	0·0121
4/9 (H+I) ...	0·0274	...	0·0162

Time in days.	Gas	II	I	Gas	H	I
0 (Orig. solns)	0·0	0.0344	0·02915	0·0	0·02015	0·01515
1	0·0053	0·0361	0·02295	0·00235	0·0225	0·01150
2	0·0074	0·0345	0·0212	...	...	...
3	...	...	...	0·0037	0·0240	0·0113
4	0·0080	...	0·0217	...	...	...
6	0·0089	0·0348	0·0220	...	...	...
10	0·01115	0·03365	0·0211	0·0050	0·0215	0·0112

It will be observed that the value of the iodine equivalent falls rapidly to the value 1/3 (H+I), and then does not appear to undergo further change, *the value of the hydrogen equivalent increasing simultaneously.* Assuming that the substance in solution which possesses the high hydrogen equivalent is a salt of the hydrate $\mathit{H}_4\mathrm{H}_2\mathrm{B}_2\mathrm{O}_2,\mathrm{H}_2\mathrm{O}$, the change which takes place must be represented by one of the two equations :—

$$\mathit{H}_2\mathrm{H}_4\mathrm{B}_2\mathrm{O}_2,\ \mathrm{H}_2\mathrm{O} \quad = \quad \mathit{H}_4\mathrm{H}_2\mathrm{B}_2\mathrm{O}_2,\ \mathrm{H}_2\mathrm{O}, \text{ or}$$

ℒ-hydrate β-hydrate

$$\mathit{H}_2\mathrm{H}_4\mathrm{B}_2\mathrm{O}_2,\ \mathrm{H}_2\mathrm{O} \quad = \quad \mathit{H}_4\mathrm{H}_2\mathrm{B}_2\mathrm{O}_2,\ +\ \mathrm{H}_2\mathrm{O}$$

That the first equation represents the change which takes place is proved by the fact that the ammoniacal solution which has been allowed to stand for a month, after evaporation of the liquid, leaves, as a residue, a salt of ammonia as the results of the following experiment show :—

Value of (H + I) for original solution ...	0.02455
Gram equivalents of ammonia in residue from 100 ccs. of ammoniacal solution after standing a few minutes	0.00310
Gram equivalents of ammonia in residue from 100 ccs. of ammoniacal solution after standing for one month	0.00365

From the first ammonia determination the ratio $\mathrm{NH}_3/(\mathrm{H}+\mathrm{I})$ has the value 7.9, and from the second determination the value 6.7 is obtained. As was shown in Section 8g of the paper, the value which corresponds to a mixture of two molecules of $\mathrm{H}_6\mathrm{B}_2\mathrm{O}_2$ with one molecule of $\mathrm{H}_6\mathrm{B}_2\mathrm{O}_2\ (\mathrm{NH}_4)_2\mathrm{O}$ is 9.0; but as it is difficult to avoid hydrolysis on the one hand, and the retention of ammonia by the solution which remains on evaporation of the greater bulk of the liquid on the other, only approximate results are to be expected. However, the results are sufficiently accurate to prove that in all probability there are two hydrates of the formula $\mathrm{H}_6\mathrm{B}_2\mathrm{O}_2,\ \mathrm{H}_2\mathrm{O}$, namely :—

$\mathit{H}_2\mathrm{H}_4\mathrm{B}_2\mathrm{O}_2,\ \mathrm{H}_2\mathrm{O}$ ℒ-hydrate.

$\mathit{H}_4\mathrm{H}_2\mathrm{B}_2\mathrm{O}_2,\ \mathrm{H}_2\mathrm{O}$ ϐ-hydrate.

(8h.) *The decomposition of the borohydrates on evaporating the solutions.*

The solutions on evaporation in the cold, in an exhausted flask connected with a receiver immersed in liquid air, evolve very little gas till the whole of the liquid has evaporated; but the moment the last trace of visible moisture disappears much gas is evolved. The study of the behaviour of a very large number of samples of the solution has led to the conclusion that the reactions which take place are not so simple as they were supposed to be, and that the apparent breaks in the curves representing the velocity of decomposition cannot be interpreted as in the manner suggested in the preliminary paper.

As it was found that the quantity of hydrogen evolved on evaporating the solutions and heating the residues was always somewhat less than the sum of the hydrogen and iodine equivalents, a few experiments were undertaken with a view to tracing the cause of the difference. It was found that both the residue and the distillate usually absorbed a small quantity of iodine, and that the former, on addition of dilute acid, some times evolved a trace of hydrogen. As will appear from the results of the experiments which are given below, the sum of the equivalents of the hydrogen evolved on evaporating the solution and heating the residue, the hydrogen evolved on adding acid to the residue, and the iodine absorbed by the residue and distillate respectively, are only a little less than the sum of the hydrogen and iodine equivalents. The difference may be accounted for by the fact that the hydrogen always contains a trace of hydroboron.

a.		0·01595	0·0114	0·0093	0·0134
b.		0·0102	0·0061	0·00455	0·00885
.	a + b	0·02615	0·0175	0·01885	0·02225
d.	Hydrogen evolved on evaporation and subsequent heating	0·0203	0·0158	0·01285	0·02085
e.	Hydrogen from residue with acid ..	0·00065	0·0000	0·0000	0·0007
f.	Iodine absorbed by residue	0·0026	0·0013	0·0005	0·0007
g.	Iodine abosorbed by	0·0008	0·0007	0·0004	0·0004
h.		0·02435	0·0178	0·01375	0·02265

The velocity of decomposition at the ordinary temperature and at 100°, of the residues obtained on the evaporation of a large number of solutions was determined, but on carefully considering the results it appears that no definite information is to be, deduced from them. The rate of decomposition appears to depend upon a number of factors, and varying results can be, obtained with samples of residue from the same solution, under different conditions. The results obtained with the residues from three different solutions may be given as examples.

Hydrogen equivalent	...	0·01340	0·01765	0·03520
Iodine equivalent ...	...	0·00885	0·00905	0.03065
H + I ...	...	0·02225	0·02905	0·06580

Time in hours.			Gas evolved.	
1 ...	.	0·00630		
2 ...	...	0·00810	...	0·02330
3 .,.	...	0·00885		
4 ...	...	...	..	0·02515
6 ...	...			
15 ...				
20 ,,.	...			
45 ...	...	...	0·01705	0·03025
111 ...		.....		0·03185
149	...	.	...	0·032 fill

The quantity of gas which is immediately evolved when the solutions are evaporated to dryness is generally approximately equal to one half of the hydrogen equivalent, and the limiting value of the quantity which is evolved on standing is also approximately equal to the hydrogen equivalent, but the results are too indefinite for it to be quite certain whether there is any direct connection between these factors.

When the bulb containing the residue was heated to 100° quantities of gas were given off which varied considerably with samples of the residue from the same solution, and no conclusions could be arrived at from the results.

(9). *Solutions of Class B, which contain excess of magnesium metaborate.*

So far we have shown that the solution which is obtained by the action of water on the magnesium boride, prepared as as described in Section 2 of this paper, contains as as its principal constituents the compounds $H_4H_2B_2O_2$ and $H_2H_4B_2O_2$ MgO. On addition of ammonia to the solution, magnesium hydroxide is precipitated, and an ammonia salt $H_2H_4B_2O_2\ (NH_4)_2O$, is formed, which, on standing, appears to change into the more stable β-modification, $H_4H_2B_2O_2\ (NH_4)_2O$. These solutions contain no magnesium metaborate.

When water acts upon magnesium boride, which has not 'deflagrated' in the course of the process of preparation, or upon a mixture of the boride, which has been properly prepared, with free boric acid, a solution is obtained for which the value of the iodine equivalent is greater than that of the hydrogen equivalent, the value* of the ratio I/H approaching 2 as a limiting value. These solutions always contain excess of magnesium metaborate, and are invariably deep yellow in colour, owing to the presence of colloidal boron.

On adding ammonia to the solutions a considerble precipitate of magnesium metaborate is immediately thrown down. If the hydrogen and iodine equivalents of the solutions are determined immediately after adding ammonia, it is found that the hydrogen equivalent has increased and the iodine equivalent has fallen in value by approximately the same amount. Thus:—

Hydrogen equivalent of original solution ...	0·00720
Iodine equivalent of „ „ ...	0·0123
(H + 1)	0·0195
Hydrogen equivalent of ammoniacal solution	0·01025
Iodine „ „ „ ...	0·01130
(H 4 I)	0·02155

The difference between the sum of the equivalents for the two solutions being due to secondary changes in the solutions. If the solution is evaporated in vacuo to small bulk, is allowed to stand, or* is heated, the change proceeds further. Thus after concentrating the solution used in the above experiment in vacuo, we found:—

Hydrogen equivalent of concentrated solution	0·0126
Iodine „ „ „ „	0·0060
(H 4 T)	0·0186

The effect of warming the ammoniacal solution appears from the result of the following experiments:—

Original solution.

Hydrogen equivalents	...	0 00985	0·0075
Iodine equivalents	...	0 01145	0·0116
H + I	...	0·0213	0·0191
Boron ...	...	0.158	
Magnesium ...	...		

Ammoniacal solutions after

Hydrogen equivalent	...	0·0131	00127.1
Iodine equivalent	..	0 00825	0·00915
H + I	...	0 02135	0·0169
Boron ...	...	0·079	0·065
Magnesium ...	...		

The quantities of boron and magnesium present in the

are expressed in gram-atoms per 100 ccs. of solution. Ho far as the hydrogen and iodine equivalents are concerned the change which takes place may apparently be expressed by the equation :

$$H_4H_2\cdot X;$$

loss of hydrogen, and other secondary changes, accounting for the irregularities in the experimental results. The experiments throw no light upon the relationship between the values of the hydrogen and iodine equivalents, and the quantities of boron and magnesium in combination with the hydrogen.

We were quite unable, by chemical n

the excess of magnesium borate, and free boric acid, from the solutions; but a physical method, which we will now describe, enabled us to obtain an almost complete separation of these impurities. This method is based upon the fact that magnesium metaborate solutions tend to crystallise, forming an almost insoluble hydrated metaborate.

Quantities of the solutions, which had previously

analysed, were sealed up in exhausted tubes with excess of magnesium hydroxide, obtained by precipitating a solution of the nitrate with ammonia, washing the precipitate thoroughly with ammonia solution, and drying it in vacuo. The tubes were agitated continuously for several days, and were then opened, and the contents analysed. The following are the results of the experiments :—

Experiment No. 1.

	Time in days.	H Equiv.	I Equiv.	Gas in tube.	B.	Mg.
a.	0	0·01905	0·03235	0·0	0·114	0·023
b.	1	0·01875	0·02995	0·00195	0·0195	0·0046
c.	2	0·01855	0·02965	0·0024	0·0228	0·0019
b.	4	...	...	...	0·0212	0·0050

It is obvious from the results of this, and of subsequent experiments, that a large quantity of magnesia and boric acid (*the results are, as usual, expressed in gram atoms per 100 ccs.*) is rapidly removed from the solution.

From the value of the ratio I/(H + I) it is a simple matter to determine graphically the proportions in which substances having the formulae $H_4\mathrm{H}_2$-X and $H_2\mathrm{H}_4$-X are present in the solution. As in the above case the value of the ratio is 0·63, the solution must contain 10 per cent of $H_4\mathrm{H}_2$-X and 90 per cent of $H_2\mathrm{H}_4$-X. If the substances have the formula $H_6B_2O_2$, the solution should contain 0·0171 gram atoms of boron per 100 ccs, and if the compound having the low hydrogen equivalent is present as the magnesium salt of the formula $H_2\mathrm{H}_4B_2O_2$, MgO, the solution should contain 0·0077 gram atoms of magnesium per 100 ccs. Assuming that the excess of boron over that required to form the compounds $H_6B_2O_2$ is present as magnesium metaborate, it is possible to calculate the quantity of magnesium present in combination with the boric acid, and, by difference, the quantity present combined with the hydrate of the borohydrate. Thus :—

	Boron as borohydrate.	Boron as metaborate.	Magnesium as metaborate	Magnesium combined with borohydrate.
b.	0·0171	0·0024	0·0012	0·0034
c.	0·0171	0·0058	0·0029	0·0020
d.	0·0171	0·0041	0·0020	0·0030

As might be expected the results are somewhat irregular. However, it will be observed that in one tube (b) the excess of boron over the quantity theoretically required for the compounds of the formula $H_6B_2O_2$ is only about 14 per cent. The total magnesium in the solutions which had been agitated with magneisum oxide is less than that required for the saturation of the hydrate, $H_2H_4B_4O_2, H_2O$; which is more than twice the quantity of the magnesium uncombined with boric acid,

Experiment 2.

Time in days.	II Equiv.	I Equiv.	Gas in tube.	B.	Mg.
0	0·0108	0.0183	0 0		
2			0.002 15	0·0099	0·0030
4	0·01275	0·01375	0·00295	0·0099	0·0030

Value of

Solution contains 10 per cent of H_4H_2—X and 90 per cent H_2H_4—X.

For $H_6B_2O_2$ the concentration of the boron should be, 0.0097, and if the compound H_2H_4—X is present as a magnesium salt the concentration of the magnesium in the solution should be 0.00435. It appears that in this experiment nearly the whole of the magnesium metaborate separated from the solution, but again the quantity of magnesium in solution is less than that required to combine with the compound $H_2H_4B_2O_2, H_2O$.

Experiment 3.

In this experiment the solution (55 ccs.) was shaken for two days with magnesium oxide. The solution was then filtered, and a quantity of it (25 ccs.) was shaken for two days with fresh magnesium oxide,

	Time in days.	II Equiv.	I Equiv.	Gas in tube.	B.	Mg.
a	0	0·03595	0·0602	0 0	0·054	0·0128
b	2	0·0310	0·0508	0·0087	0 038	0 0071
c	4	0·0354	0·04725	0·0117	0·033	0 0067

The value of (II+I) for the original solution is 0.09875 which is about 4 per cent higher than the values for the solutions which have been shaken with magnesium oxide. The boron content, calculated from the first value (maximum) should be 0.033 gram atoms per 100 ccs, which is the smallest value obtained (c), and calculated from the second (minimum) value should be 0.031. Supposing that the compound H_2H_4—X. is present as the magnesium salt, the magnesium content of the solution should be 0.0049 gram molecules of MgO per 100 ccs. It is found that, supposing that the excess of boric acid in the second solution (b) is present as magnesium borate, the remaining magnesium, which must he present in combination with the boro-hydrate, is exactly equal to this quantity. In the third solution (c), which was shaken with fresh magnesium oxide, the boron present as bane. acid is probably not more than 0·002 gram atoms per 100 ccs, which is equivalent to O'OOI gramatoms of magnesium oxide per 100 ccs. The quantity of magnesium oxide present as the salt of $H_6B_2O_2$, H_2O_2 appears, therefore, to ho at least 0·0057 gram molecules por 100 ees, which is somewhat in excess of the quantify calculated from the value of $(H+I)$ on tho supposition that tho original solution contained 90 per cent of $H_2H_4B_2O_2$, H_2O_2 (α) as the magnesium salt and 10 per cent of $H_4H_2B_2O_2$. If however the solution really contains, besides $H_2H_4B_2O_2$, H_2O (α), not $H_4H_2B_2O_2$, but the fl-hydrate, $H_4H_2B_2O_2$, H_2O, as the magnesium salt, the magnesium content should be 0.0055 gram molecules of MgO por 100 ccs, which is very close to the 0,0057 figure given above.

From these experiments it, is quite clear that the relationship between the hydrogen and boron present in combination in the solutions of Class B, which also contain originally much magnesium metaborate, is the same as in the compounds which exist in the solutions of Class A, and is expressed by tho formulae $H_6B_2O_2$, and $H_6B_2O_2$, H_2O. The solutions may
am: ••

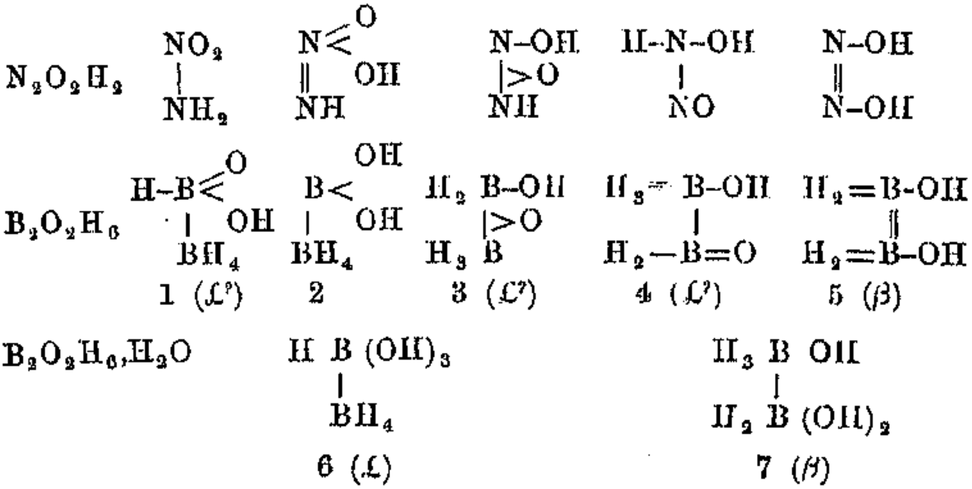
a. $H_4H_2B_2O_2$ α-Hexahydro-dioxy-dil oron
b. $H_2H_4B_2O_2$ β-Hexahydro-dioxy-diboron
c. $H_4H_2B_2O_2$, H_2O α-Hexahydro-dioxy-diboron, hydrate

d. $H_2H_4B_2O_2$, H_2O β-Hexahydro-dioxy-diboron, hydrate

It is obvious that the greater part of tho borohydrate in tho original solution is the substance *c*, which is present to the extent of one-third of the total borohydrate in the solutions of Class A. Whether the compound *a* is present at all appears to be doubtful, fur when large excess of magnesium oxide is present in contact with the solution, the quantity of magnesium taken up is at least sufficient to combine with the. whole of the borohydrates calculated as $H_6B_2O_2$, H_2O. From the last experiment it, also appears probable that the, borohydrate of tho formula H_4H_2-X is the β-hydrate, $H_4H_2B_2O_2$, H_2O and not the compound $H_4H_2B_2O_2$. If this is the case it is also probable that the borohydrate which is originally present in solutions of Class B is the compound $H_4H_2B_2O_2$, H_2O, which undergoes spontaneous change to a slight oxtent into the β-compound $H_2H_4B_2O_2$, H_2O, and which is changed completely info tho latter compound on standing with ammonia solution.

10. *The constitution of the borohydrates.*

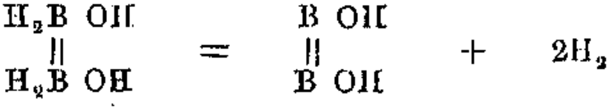
We may now proceed to show how it is possible to account for and explain the existence of ℒ-and β-hexahydro-dioxy-diborons, and of the ℒ-and β-hydrates. The compounds are without doubt reduced and hydrated derivatives of compounds, which are analogous to the compounds nitro-amide and hyponitrous acid, or to the hypothetical compounds which are intermediate between them. Thus:



$$\begin{array}{llllll}
 & NO_2 & N\overset{O}{<}OH & N{-}OH & H{-}N{-}OH & N{-}OH \\
N_2O_2H_2 & | & \| & |{>}O & | & \| \\
 & NH_2 & NH & NH & NO & N{-}OH \\
 & H{-}B\overset{O}{<}OH & B\overset{OH}{<}OH & H_2\,B{-}OH & H_2{=}B{-}OH & H_2{=}B{-}OH \\
B_2O_2H_6 & | & | & |{>}O & | & \| \\
 & BH_4 & BH_4 & H_3\,B & H_2{-}B{=}O & H_2{=}B{-}OH \\
 & 1\ (ℒ?) & 2 & 3\ (ℒ?) & 4\ (ℒ?) & 5\ (\beta) \\
B_2O_2H_6,H_2O & H\ B\,(OH)_3 & & & H_3\ B\ OH & \\
 & | & & & | & \\
 & BH_4 & & & H_2\ B\,(OH)_2 & \\
 & 6\ (ℒ) & & & 7\ (\beta) &
\end{array}$$

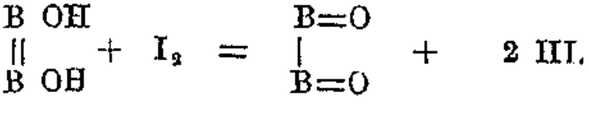
That boron is either tetravalent, or pentavalent and capable of forming compounds with doubly linked boron atoms, is supported by the work of Stock and Frederici (Ber., XXXXVI, 1959), since the compounds B_2H_6 and B_4H_{10}, which they have described, can be represented by the graphic formulae $BH_3{=}BH_3$ and $BH_3{=}BH_2{-}BH_2{=}BH_3$. It appears also to be probable that symmetrical compounds of the form $={B}{=}{B}=$ are the most stable.

There is no doubt that the β-hexahydro-dioxy-diboron must be assigned the formula 5 which contains the group of which is indicated above. On treatment with acid it forms a compound analogous to hyponitrous acid, thus :—



$$\begin{array}{l}H_2B\ OH\\ \ \ \|\\ H_2B\ OH\end{array} = \begin{array}{l}B\ OH\\ \|\\ B\ OH\end{array} + 2H_2$$

on treating the acid solution with iodine



$$\begin{array}{l}B\ OH\\ \|\\ B\ OH\end{array} + I_2 = \begin{array}{l}B{=}O\\ |\\ B{=}O\end{array} + 2\ HI.$$

If the ℒ-hexahydro-dioxy-diboron does actually exist, as appears to be possible, though it is certainly unstable, it must have the formula represented by 1, 3, or 4, as in either of these eventualities two atoms of hydrogen could be removed, and the resulting compound would be represented by a formula containing the group B=B. The fact that the solutions, on treatment with acid always yield traces of a hydroboron of low boiling point, which has not been isolated, may be accounted for by assuming the existence of the group$=BH_3$ or $-BH_4$ in one of the compounds present in the solutions. However, it is probable that the latter group is present in the ℒ-hydrate.

It appears that there can only be two hydrates of the formula $H_6B_2O_2, H_2O$, which are represented by the structural formulae 6 and 7. Formula 6 probably represents the structure of the ℒ-hydrate, which appears to be a normal constituent of the solution obtained by the action of water on the magnesium boride prepared as described in Section 2 of this paper. On treating the solution with acid this compound loses two atoms of hydrogen, thus :—

$$\begin{array}{c} HB(OH)_3 \\ | \\ HBH_3 \end{array} \quad = \quad \begin{array}{c} B(OH)_3 \\ \| \\ BH_3 \end{array} \quad + \quad H_2$$

On treating the solution with ammonia the ℒ-hydrate appears to be transformed into the β-hydrate, and this compound, the structure of which is represented by formula 7, on treatment with acid loses four atoms of hydrogen, thus :—

$$\begin{array}{c} H_2B(OH)_2 \\ | \\ H_3B\,OH \end{array} \quad = \quad \begin{array}{c} B(OH)_2 \\ | \\ HB\,OH \end{array} + 2\,H_2$$

(11) *The probable existence of an oxide lower than B_2O_2.*

When the solution of the borohydrates was made strongly alkaline with ammonia, the magnesium present in it was completely precipitated as hydroxide (p. 15). On evaporating the solution and heating the residue a product was left which consisted mainly of the oxide B_2O_2, but on dissolving this residue in water and treating the residue with dilute hydrochloric acid a very small quantity, not exceeding 5 per cent of the whole, remained undissolved. The residues from two series of experiments were collected separately and analysed. The substance dried at 100°, was weighed, and the loss of weight and quantity of hydrogen evolved on heating were determined. The residue was then dissolved in nitric acid, and the insoluble portion was collected on a filter and weighed. The boron was then determined in the acid solution. The following are the results of the experiments:—

	A.	B.
Loss of weight on heating	0·0134	0·0029
Water equivalent to the hydrogen given off.	0·0072	0.0053
Total water	0.0206	0·0082
Weight of residue after heating	0·0614	0·0276
Weight of portion soluble in HNO_3.	0·0638	0·0253
Oxygen equivalent to the hydrogen given off.	0·0063	0·0046
Weight of lower oxide (anhydrous).	0·0575	0·0207
B_2O_3	0·0928	0·0354
B_2O_3 from 1 gram of oxide	1·61	1·71
H_2O from 1 gram of oxide	0·35	0·38

The oxide is insoluble in strong hydrochloric acid and in caustic alkali solution, but readily dissolved in moderately dilute nitric acid, being converted at the same time into boric acid. From the results of the analyses it appears that substance is slighty impure hydrated tetraboron trioxide, of the formula B_4O_3, 2 H_2O, for which the results of analysis should show :—

1 gram of B_4O_3 equivalent to 1,52 grams B_2O_3,
1 gram of B_4O_3 equivalent to 0.39 grams H_2O.

If the impurity consisted of traces of amorphous boron, as is most highly probable, part of which would dissolve in dilute nitric acid, it would account for the high values of the boric acid obtained from the oxide.

(12) *Summary and conclusions.*

(1) When magnesium boride is treated with water the main product of the reaction is a compound of the formula $B(H_2O)n$, together with magnesium oxide, the two being in combination in unknown proportions.

(2) When proper conditions are observed in preparing the boride, the solution obtained on treating it with water in the cold is free from magnesium metaborate, but contains substances, called borohydrates, which are compounds of boron, hydrogen and oxygen.

(3) The solution referred to above contains the magnesium salt of a compound $H_2\mathrm{H}_4\mathrm{B}_2\mathrm{O}_2$, $\mathrm{H}_2\mathrm{O}$, α-hexahydro-dioxy-diboron hydrate, together with a compound $H_2\mathrm{H}_4\mathrm{B}_2\mathrm{O}_2$ (3-hexahydro-dioxy-diboron. It appears that traces of an unstable compound ff$_2$I-I$_4$B$_2$0$_2$ α-hexahydro-dioxy-diboron may also be present, though this is uncertain.

(4) On treating the solution with ammonia, magnesium hydroxide is precipitated, and the ammonia salt of the hydrate is obtained. On standing this is transformed into the β-hydrate $H_4\mathrm{H}_2\mathrm{B}_2\mathrm{O}_2$.

(5) if the boride contains free boric acid the solution which is obtained by the action of water upon it contains much magnesium metaborate in solution. It appears probable that the original solution contains only, in addition to this compound, the α-hydrate $H_2\mathrm{H}_4\mathrm{B}_2\mathrm{O}$, $\mathrm{H}_2\mathrm{O}$, as the magnesium salt. This compound undergoes partial spontaneous transformation into the β-hydrate, into which it is completely changed on standing with ammonia solution.

(6) The solutions have the peculiar property of evolving hydrogen when treated with acids, or when brought into contact with porous substances

(7) Two new oxides of boron $\mathrm{B}_2\mathrm{O}_2$ and $\mathrm{B}_4\mathrm{O}_3$ are also described.

In conclusion we have to thank Mr. Syed **Bashirodeen** for his assistance in carrying out this work.