

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 the preparation of the boride was worked out, and the 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 be increased by varying the proportions in which the magnesium powder and boric acid were present in the mixture from which the boride was prepared, and negative* results had been obtained, the study of magnesium boride was taken up by one of us (H. C. K.). The results of these experiments, which will be published separately, tend to prove that there is only one boride of magnesium, which has the formula Mg_3B_2 . In practice we find that the best method for preparing the boride for the purpose of these experiments is to heat a mixture 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 reaction 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 metaborate.

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

The results of the experiments described in this section of the paper prove that magnesium borate 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 water, placed the flask containing the mixture in a bath of ice water. In certain experiments the hydrogen which was 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 at 0° and 700, mm.
0	0
2	2,850
17	3,480
	5,100
65	7,920
89	10,400
113	32,080
137	1,3080
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 gram 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 may 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.), but 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 :—

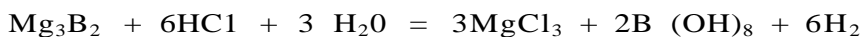
Magnesium	0.6773 grams.
Boron	0.0718 ,,
Oxygen (diff.)	0.2300 ,,
Residue (boron, insoluble in HCl)	0.0209 ,,

The quantity of boron in 1 gram of the original mixture, calculated from the "boric oxide contained in it, was 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 has generally been assumed to be the case, is formed according to the equation:



The following experiment shows that the soluble boron is present practically entirely as the boride, 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_2 , 1 gram of the impure boride should according to the equation:



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:



The main product being a magnesium derivative of a compound of the formula, $\text{B}(\text{H}_a\text{O})_n$ 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	0.0280	gram
of boron soluble in dilute nitric acid,		
1 gram of the residue gave	0.0077	gram
of hydrogen with dilute hydrochloric acid.		

From 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 boride 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, which 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 far as the evolution of the gas is concerned, but on treating it with hot or cold water, no further quantity of soluble borohydrate is produced.

4. *Magnesium Meta-borate.*

In the course of this research we have found it necessary to investigate the properties of magnesium metaborate, 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 $Mg(BO_2)_2$. 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.

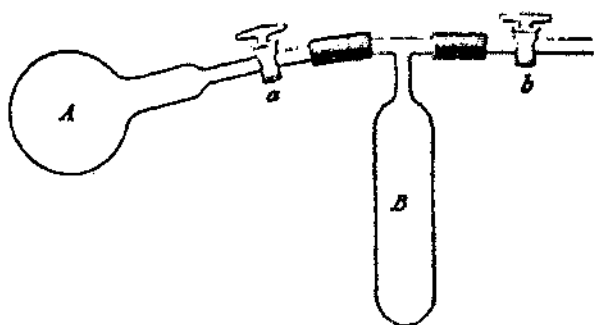
5. *Methods of analysis.*

As the solutions contained only magnesium and boron, in combination with hydrogen and oxygen, the determination of these elements was a comparatively simple matter. The magnesium was 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 acid, 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 the 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.



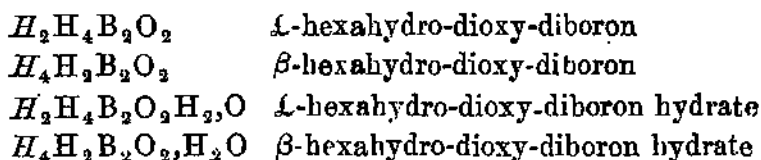
The hydrogen evolved on addition of acid was determined by introducing a measured quantity of the liquid into a distillation flask of about 75 ccs. capacity, fitted with a tap funnel. The flask was connected with a Töpler pump, and after exhausting it, about 15 cc. of 30 per cent sulphuric acid was run 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 :



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 metaborate.*

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 preliminary 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-four hours in contact with that reagent in acid solution, and did not appear to react with oxidising agents. When the contents of the bulb 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 difference 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, less 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	1.50

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:—

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

(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_3 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 solution 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_2 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 aniuooniacal solulicon 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,

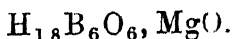
(86'). *The results of analysis of solutions of the borohydrates which are free from magnesium metaborate.*

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 iirst 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.

(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 between 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 empirical formula,



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 (but 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 $(\text{H}_3\text{BO})_n$ 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 ₃ BO) _n in original solution		0·2155	0·2225	0·1625
MgO	,,	0·0497	0·0494	0·0361
(H ₃ BO) _n in solution used		0·2155	0·1480	0·1080
MgO	,,	0·0497	0·0329	0·0240
Depression of freezing point		0·090°	0·065°	0·045°

The molecular weights (mean) of the residue (H₃BO)_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 (H₃BO)_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 H₆B₂O₂, 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, B₂O₃. 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 small quantities of the boron oxide are liable to be carried with the vapours. This loss of boron can 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. The following are the results of some of the experiments:—

Hydrogen equivalent + iodine equivalent	0.1048	0.0558	0.0394	
Residue from 100 ccs. of solution	0.581	0.488	0.379	0.252
B ₂ O ₃ from residue	0.114	...	0.485	0.324
Boron in gram atoms	0.0318	0.0181	0.139	
(H + I)/3B	1.09	1.03	0.94	

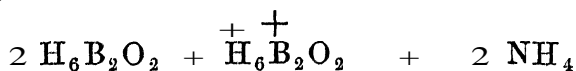
These results taken with the results of the analyses of the solutions containing magnesium, tend to prove that the solutions from which the magnesium has been precipitated by ammonia contain boron, hydrogen, oxygen and the elements of ammonia and water, combined in the proportions H_{1.8}B_{0.6}O₆, (NH₄)₂O, but that hydrolysis and loss of ammonia on evaporation.

(8h) *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 $(\text{H}_3\text{BO})_n$, was evaporated nearly to dryness at the air temperature, and redissolved in a known quantity of water. The freezing point of the solution was then determined and compared with the freezing point of pure water. The following are the results of the experiments :—

$(\text{H}_3\text{BO})_n$ 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 :—



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 $(\text{H}_3\text{BO})_n$ 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.

8i. *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.

Sj. 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 under 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 :—

Time.	Liquid in sealed tubes.			Liquid in flask exposed to the air.	
	• 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

of the proportion in which they are present can be determined from the value of the ratio

Proportions in which the compounds are	of Ratio	+ 1)
a. Only $\text{fi}''_4\text{H}_2\text{-X}$		
b. $\frac{2}{3}$ — $\frac{1}{3}$		
$\text{ff}_4\text{H}_2\text{-X}$ —		
d. Only		0.66

the figures set down in Table it is impossible to arrive at a definite decision as to whether the normal composition of the mixture is represented by 5 or 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 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 and the hydrogen and iodine equivalents of the solutions afterwards determined. The solutions were kept at 25° during the experiments. A very large of experiments were carried out, and the results of a selection of them, for which the value of $(\text{H} + \text{I})$ 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 $\frac{4}{9}(\text{H} + \text{I})$, and those on the right hand side of the plate are the values of $\frac{1}{3}(\text{H} + \text{I})$. 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.