

CC.—*Magnesium Boride and Amorphous Boron.*

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THE object of the present investigation was to determine whether, as Winckler (*Ber.*, 1890, **23**, 772) and Moissan (*Compt. rend.*, 1892, **114**, 392) have suggested, there might exist borides of magnesium other than the boride  $Mg_3B_2$ . Preliminary experiments were carried out in which boron trioxide and magnesium powder were heated in varying proportions, and to different temperatures. However, so far as could be ascertained from the analyses of the products, and from the action of water and acid on them, no other boride could be obtained by this method. When a mixture of 1 part of boron trioxide was heated with  $2\frac{1}{4}$  parts of magnesium powder to a red heat in a current of hydrogen for forty-five minutes, a product was obtained which was almost completely soluble in dilute hydrochloric acid, and appeared, from the results of analyses, to consist of magnesium boride,  $Mg_3B_2$ , and magnesium oxide in the theoretical proportions. If this product was heated to a higher temperature, or for a long time at a red heat, magnesium was driven off, and a mixture of amorphous and crystalline boron separated. Free boron was always obtained if excess of boron trioxide was used, and if excess of magnesium was employed, the product had a metallic appearance, and seemed to contain free magnesium.

After completing these preliminary experiments the preparation of magnesium boride from magnesium and boron was attempted, and as it was found that crystalline boron and magnesium did not enter into combination, when they were heated together, the experiments were carried out with amorphous boron. The magnesium and boron were heated together in an iron vessel, which was lined with a mixture of magnesia with a little boric acid. The vessel was fitted with a screw cap, and a rapid stream of hydrogen was passed through it from the commencement of the experiment until the apparatus had become quite cold. The vessel was heated to a bright red heat.

On analysing the product of the reaction, it was found that it always contained from 8 to 9 per cent. of oxygen, and as the only possible source of this oxygen was the substance which was supposed to be amorphous boron, it was necessary to carry out a series of experiments to determine whether this was actually the case.

Moissan (*loc. cit.*), who described a method of preparing amorphous boron by the reduction of boron trioxide with mag-

nesium powder, stated that the product contained as much as 95 per cent. of boron. In 1909 Weintraub (*Trans. Amer. Electrochem. Soc.*, **16**, 165) carried out an investigation on the same subject, but as this journal was not available in Bangalore, and as the paper was not abstracted into other journals, I was not acquainted with the results of his experiments until after the completion of my own work. He found that the so-called amorphous boron always contained oxygen, and drew the conclusion that it is really a suboxide. However, Weintraub's paper does not contain a single complete analysis of the amorphous boron; and my own results and conclusions differ from his in certain important particulars.

In preparing the boron the mixture of magnesium and boron trioxide or borax was heated in a crucible through which a rapid current of hydrogen was passed. After cooling, the contents of the crucible were treated repeatedly with hot and moderately dilute hydrochloric acid. The product was then washed with water and dried in a desiccator. Finally, the powder was placed in a hard glass tube, which was connected with a mercury pump, and heated to the softening point of the glass. The following are the results of the analyses, and certain particulars with regard to the preparation of the various samples:

Composition of mixture.	I.	II.	III.	IV.
B <sub>2</sub> O <sub>3</sub> .....	1	1	3	3
Mg .....	2½	2½	1	1
Time of heating.....	1 h. 20 m.	1 h. 20 m.	30 m.	30 m.

*Analysis of Product.*

Boron soluble in dilute nitric acid .	67.41	64.12	75.88	64.08
Boron insoluble in dilute nitric acid .	4.04	9.42	5.23	2.71
Mg .....	3.39	7.58	2.36	11.12
O (by difference) ...	25.16	18.88	16.53	22.09

Composition of mixture.	V.	VI.
Borax .....	1	5
Mg .....	1	4
Time of heating .....	1 h. 40 m.	1 h. 20 m.

*Analysis of Product.*

Boron soluble in dilute nitric acid.....	52.60	61.93
Boron insoluble in dilute nitric acid.....	20.94	3.90
Mg .....	7.68	9.97
O (by difference) .....	18.78	24.20

Weintraub does not appear to have made any distinction between the "amorphous boron," which is readily soluble in warm dilute nitric acid, and the crystalline boron, which is always present in smaller or larger quantity, and is insoluble in nitric acid. With regard to the magnesium content of the product he refers to the fact that samples containing less than 1 per cent. of magnesium had been obtained by heating mixtures of 4 parts of boron trioxide with 1 part of magnesium, and to the complete removal of the magnesium when the "boron suboxide is re-fused at high temperature with boric anhydride" in the electric vacuum furnace. The product then obtained is said to contain 16 to 14 per cent. of oxygen, but no analyses are given. This point will be discussed later.

The object of the present investigation was to obtain amorphous boron, which should be free from oxygen, and, therefore, samples of the substance containing oxygen were heated with excess of magnesium, and with metallic sodium. In the first case, magnesium boride was formed, and subsequently decomposed at the higher temperature employed. The final product in each case was crystalline boron, which was insoluble in nitric acid, and did not combine with magnesium to form a boride. The following are the results of the analysis of one sample of the crystalline boron:

Boron .....	98.10
Silicon .....	2.16
Magnesium .....	Trace
Total .....	100.26

It would appear that the substance which Weintraub considers to be boron suboxide, and has generally been supposed to be amorphous boron, is really a solid solution of a lower oxide of boron, in boron. This view is supported by the fact that, as Travers and Gupta have shown, an oxide, which has the formula  $B_4O_3$ ,\* and is insoluble in acids or alkalis, actually exists, and also by the work of Louis (*Diss.*, Stuttgart), who has shown that the so-called monoxide of zirconium is possibly a solid solution of a dioxide in the amorphous element. It is not at all improbable that amorphous substances, which must be regarded as supercooled liquid, are only stable when they contain impurities. As will be shown presently, the magnesium in the substance is probably present as the oxide, possibly as a borite in solid solution. If this is assumed to be the case, the atomic ratio of the boron, which is soluble in nitric acid, to the oxygen which is not

\* Communicated to the Royal Society.

combined with the magnesium, is found to have a fairly constant value:

No. of experiment.	I.	II.	III.	IV.	V.	VI.
Ratio B/O .....	4.2	6.6	6.6	6.1	5.2	5.2

One would expect the results to be more concordant if the substance were a compound, such as a suboxide. Further, the existence of an oxide,  $B_2O_3$ , does not appear to be likely.

Fairly conclusive evidence that the magnesium is present in combination with oxygen, and not in combination with boron, is derived from certain experiments, which were carried out with the view of testing Weintraub's statement that the magnesium could be removed by fusion with boron trioxide. Two samples of the amorphous boron were taken for these experiments, one of them containing a small, and the other a large, proportion of crystalline boron. The following are the results of the experiments:

*Experiment A.*

	Before fusing with boron trioxide.	After fusing with boron trioxide.
Boron insoluble in $HNO_3$ .....	2.71	3.12
Boron soluble in $HNO_3$ .....	64.08	77.35
Mg .....	11.12	0.58
O (by difference) .....	22.09	18.95
Ratio B/O (combined with B) .....	6.10	6.02

*Experiment B.*

Boron insoluble in $HNO_3$ .....	20.94	20.18
Boron soluble in $HNO_3$ .....	52.60	58.41
Mg .....	7.68	3.23
O (by difference) .....	18.78	18.18
Ratio B/O (combined with B) .....	5.20	5.30

In calculating the value of the ratio B/O (combined with B), it is assumed that the magnesium is present in both cases as the oxide  $MgO$ . As this ratio remains practically unchanged, even when nearly the whole of the magnesium has been removed, it is obvious that the removal of the magnesium must have been accompanied by the removal of oxygen, that these two elements were present in the system in combination, and that the magnesium was not present as a boride. That the magnesium is not removed by heating the amorphous boron with hydrochloric acid in a sealed tube to  $150^\circ$ , whilst it is readily removed by fusion with boron trioxide, may be explained by the fact that the rate of diffusion of the magnesium oxide in the "solid" solution is very much greater at the higher than at the lower temperature.

It should, furthermore, be pointed out that on heating the samples of boron which were prepared from borax they evolved

a considerable quantity of hydrogen, but that the loss of weight on heating was only equivalent to the weight of hydrogen lost. The atomic ratio of the hydrogen to the total oxygen is in the first case  $1/1.3$  and in the second case  $1/3$ . In both cases the atomic ratio of the boron soluble in nitric acid to the total oxygen is the same, namely,  $5.2$ , and this, together with the fact that the loss of weight is equal to the weight of the hydrogen lost, makes it probable that the hydrogen is actually occluded in the substance, and is not originally present as water. Thus from 1 gram of substance there was obtained, in the case of No. V, 0.009 gram of hydrogen, and 0.004 gram in the case of No. VI. The samples of boron prepared from boron trioxide gave off only a trace of gas.

It will be observed that both the samples of amorphous boron which yield hydrogen on heating contain a large quantity of crystalline boron, and that it is the crystalline boron which occludes the hydrogen appears, from the following experiment, to be highly probable. A quantity of amorphous boron, containing about 3 per cent. of crystalline boron, which yielded only a trace of hydrogen when heated, was heated strongly with a small quantity of magnesium, and the residue, after treating with hydrochloric acid, and washing with water, was dried in a vacuum overnight. The residue, containing 30 per cent. of crystalline boron, was dried in a desiccator for a day, and the quantity of hydrogen which was given off on heating was determined. Further determinations of the quantity of hydrogen evolved on heating were made after sixteen and seventy-two days. The following are the results of the experiments:

Time.	Quantity of hydrogen per cent.
1 day.....	0.52
16 days .....	0.46
72 „ .....	0.34

As might be expected the occluded hydrogen is slowly oxidised when the boron is exposed to the air.

### *Magnesium Boride.*

As it was found that no change took place when crystalline boron was heated with magnesium, that it was impossible to obtain amorphous boron free from oxygen, and that magnesium boride decomposed when heated strongly into magnesium and boron, it was obviously impossible to obtain the boride in the pure state, but only a mixture of the boride with magnesium oxide and a small quantity of crystalline boron. However, by investigating the reaction between magnesium and the amorphous boron, and

making a series of analyses of the products, it was possible to arrive at a definite conclusion as to the composition of the one boride which appears to exist.

In these experiments the samples of amorphous boron I and III, of which the analyses are given above, were employed. The brown powder was packed tightly between two layers of magnesium powder into the magnesia-lined iron crucible. The cover was then screwed on to the crucible, which was heated to a red heat for about half-an-hour, a rapid current of hydrogen being passed into it from the commencement of the experiment until the apparatus was cold. The crucible was then opened, and the mass of boride was separated without difficulty from the two plates of metallic magnesium which lay above and below it. It was then crushed and analysed. The following are the results of the analyses:

	I.	II.	III.	IV.	V.
Insoluble in nitric acid.....	3.82	2.42	1.03	0.76	0.76
Insoluble in hydrochloric acid .	3.86	2.48	1.10	0.80	—
Magnesium .....	70.16	74.48	73.33	72.99	74.13
Boron soluble in nitric acid.....	17.19	14.82	16.76	18.48	18.76
Oxygen (by difference) .....	8.83	8.28	8.88	7.77	6.35
Magnesium as oxide .....	13.23	12.42	13.32	11.64	9.51
Magnesium as boride, or as metal (A) .....	56.93	62.06	60.01	61.35	64.62
Boron as boride (B) .....	17.19	14.82	16.76	18.48	18.76
Ratio A/B .....	1.5/1	1.9/1	1.6/1	1.5/1	1.5/1

In this series of experiments it will be observed that the difference between the amount of the residue insoluble in nitric acid and of the residue insoluble in hydrochloric acid is extremely small, showing that the whole of the boron was present either as boride, or as crystalline boron. It is, therefore, certain that not more than 1.5 gram-atoms of magnesium is required to combine with 1 gram-atom of boron. Further, when the ratio  $A/B$  rose much above 1.5, as in the case of experiment No. II, the residue had a metallic appearance, and obviously contained metallic magnesium.

In order to determine whether a boride containing less magnesium than the compound  $Mg_3B_2$  could exist under the conditions under which these experiments were carried out, samples of product No. II were heated for increasing periods in a vacuum in quartz tubes. The following are the results of the experiments:

	II.	IIa.	IIb.	IIc.
Insoluble in nitric acid.....	2.42	2.51	4.60	8.55
Insoluble in hydrochloric acid.....	2.48	2.48	6.30	12.23
Magnesium .....	74.48	72.44	68.02	63.10
Boron soluble in nitric acid.....	14.82	15.16	16.65	15.23
Oxygen (by difference) .....	8.28	9.89	10.73	13.12
Mg as oxide .....	12.42	14.82	16.08	19.68
Mg as boride or as metal (A) .....	62.06	57.62	51.94	43.42
B as boride (B) .....	14.82	15.16	14.90	13.55
Ratio A/B .....	1.9/1	1.7/1	1.59/1	1.47/1

The results of these experiments show that on heating in a vacuum such a mixture, for which the value of the ratio  $A/B$  is much greater than 1.5, magnesium volatilises, but that, at first, the quantity of free boron does not increase. When, however, the value of the ratio falls to the neighbourhood of 1.5, the quantity of crystalline and amorphous boron in the mixture begins to increase rapidly. It may, therefore, be concluded that under the conditions of temperature and pressure at which the experiment was carried out, no boride of magnesium other than the compound  $Mg_3B_2$  can exist.

### *Conclusions.*

(1) The element boron has only been obtained in one form in a state approaching purity, namely, that of a crystalline substance which is practically insoluble in nitric acid.

(2) Weintraub's conclusion that the so-called amorphous boron always contains a considerable quantity of oxygen has been confirmed.

(3) It appears probable that the so-called amorphous boron is a solution of a lower oxide of boron and of magnesium oxide, possibly in combination as a borite, in elementary boron in the amorphous or superfused liquid state. The magnesium oxide may be removed by fusion with boron trioxide, but not by heating with acids.

(4) On heating crystalline boron with magnesium no reaction takes place, but on heating the so-called amorphous boron with magnesium, a mixture of magnesium boride ( $Mg_3B_2$ ) and magnesium oxide is obtained.

(5) At a red heat and under normal pressure only one boride having the formula  $Mg_3B_2$  is formed.

(6) On heating the boride, magnesium is driven off and the greater part of the boron separates in the crystalline state.

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