

XII.—*The Atomic Weight of Boron.*

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Preliminary.

THE atomic weights employed in this paper are those given by Clarke:—Ag = 107·92, Na = 23·05, Cl = 35·45, Br = 79·95, H = 1·008, and O = 16.

Three estimations of the water of crystallisation in borax were made by Berzelius and two by Laurent. For the recalculation of the atomic weight of boron, Clarke, in his *Constants of Nature*, combines these five estimations, and obtains a mean percentage of water $47·13 \pm 0·013$; hence $B = 10·943 \pm 0·023$.

Berzelius also determined the atomic weight of boron by fusing borax with hydrogen fluoride and sulphuric acid; in this way he obtained $B = 10·97$.

Argvedson made some experiments upon borax with calcium fluoride and hydrogen sulphate; his results for the atomic weight of boron varied from 9·9 to 10·86, and cannot therefore be regarded as of much value (*Ann. Phys. Chem.*, **2**, 129).

Dumas (*Ann. Chim. Phys.* [3], **55**, 181) calculated the atomic weight of boron from experiments made by Deville (*Annalen*, **113**, 31, and *Ann. Chim. Phys.*, **52**, 84) upon the chloride and bromide of boron. Deville prepared boron chloride by the action of gaseous hydrogen chloride upon boron, and estimated the chlorine in the compound as silver chloride. From 0·6763 gram of boron chloride, he obtained 2·477 grams of AgCl; from this, boron chloride contained 90·6 per cent. of chlorine, and the atomic weight of boron would be 11·08.

Another analysis was made of a sample of boron chloride formed by the action of chlorine on boron; in this case, 0·9225 gram of boron chloride gave 3·395 grams of silver chloride; the boron chloride therefore contained 91·002 per cent. of chlorine; hence $B = 10·50$; mean, $B = 10·79$.

The filtrate from the first analysis was evaporated to dryness; after the excess of silver had been removed, and on treating the residue with water, the presence of a considerable quantity of silica was ob-

* Since beginning to write this paper, we received, through the kindness of the Editor, proof-sheets of Mr. J. H. Abrahall's communication on the subject. As he gives a historical introduction, it is unnecessary for us to do so, except to supplement it by a few additions.

served, showing that, along with boron chloride, silicon chloride had also been formed by the action of the hydrogen chloride on the glass.

Clarke reduces the weighings to a common standard, and finds that 100 parts of silver chloride correspond to $27\cdot303$ and $27\cdot187$ parts of boron chloride; mean, $27\cdot245 \pm 0\cdot039$; hence $B = 10\cdot808 \pm 0\cdot174$.

In the case of the bromide, $2\cdot446$ grams of boron bromide gave $5\cdot496$ grams of silver bromide; boron bromide, therefore, contains $95\cdot66$ per cent. bromine.

Clarke, including the probable error of bromine, calculates from this experiment that $B = 10\cdot964 \pm 0\cdot364$. He combines the three values thus:—

From borax	$B = 10\cdot943 \pm 0\cdot023$
„ BCl_3	$B = 10\cdot808 \pm 0\cdot174$
„ BBr_3	$B = 10\cdot964 \pm 0\cdot364$
If O = 16 then	$B = 10\cdot966$

Abrahall's Results.

When this research was commenced in November, 1891, we were unaware that any later attempts had been made to determine the atomic weight of boron; it was not till April, 1892, that the work of the late J. L. Hoskyns Abrahall came under our notice in the preliminary account published in the *Chemical News*, **65**, 215. His work has now been published in this Journal, 1892, **61**, 650. A redetermination of the atomic weight was made from the water of crystallisation in borax, but the experiments were only regarded as preliminary; the number obtained for the atomic weight varied from $10\cdot554$ to $10\cdot843$. Since the crystals of borax were allowed to stand in a vacuum over anhydrous borax for a week, there can be little doubt that slight efflorescence had taken place. It is shown later in this paper that borax exposed to the atmosphere effloresces during dry weather, and, if placed in a desiccator over sulphuric acid, loss of water to a very large extent occurs.

Abrahall's final determination of the atomic weight of borax was made by estimating the amount of silver necessary to precipitate the bromine in a given weight of boron bromide; and from these experiments he found the atomic weight of boron to be $10\cdot825$, a number lower than that given by previous observers, and lower than that obtained by us, namely, $10\cdot966$.

This discrepancy may be accounted for, in our opinion, by one or more of the following considerations:—

It is extremely probable that the boron bromide employed by Abrahall was not absolutely free from hydrobromic acid, for, as the editors of his paper state, the boron was not anhydrous, and some

hydrobromic acid must have been formed during the preparation of the boron bromide. Hydrogen bromide is not absorbed by mercury, so that it would not be eliminated by leaving the boron bromide over mercury. It is extremely probable that small quantities of a double bromide of hydrogen and boron would be formed, analogous to the double fluoride of hydrogen and boron, HF, BF_3 , or to the double fluoride of hydrogen and silicon, $\text{SiF}_4, 2\text{HF}$, or to the hypothetical double chloride of hydrogen and aluminium, the formation and instability of which explain the use of this substance in organic synthesis. The constancy of Abrahall's results is likely to be due to the double bromide distilling in definite amount with the boron bromide, just as an acid of definite strength is obtained by distilling a solution of hydrogen chloride in water. The presence of hydrogen bromide in the boron bromide would lower the atomic weight sought; the presence of less than 2 per cent. of hydrogen bromide would lower it by more than 0.141, the difference between the number obtained by Mr. Abrahall and by us.

Stas, in a paper published in 1871 in the *Comptes rendus*, **73**, 998, states that there is great difficulty in determining the end-point of the reaction with silver nitrate and sodium chloride in the method suggested by Gay-Lussac for silver assays; but, if sodium bromide or iodide is used instead of the chloride, no difficulty is found, for the end-point is distinct, and the use of bromide or iodide is therefore preferable for assays. Abrahall, on the other hand, found the determination of the end-point very difficult, and this may have led to further uncertainty.

The use of boron bromide for the basis of the atomic weight determination has the disadvantage of the great difference between the atomic weights of boron and bromine, so that, as stated by the editors of Abrahall's memoir, a given percentage error in the ratio of boron bromide to silver produces a relative error 23 times as large in the atomic weight sought.

Weighings.

The balance used in our experiments was made by Oertling. The temperature of the air in the balance case and the barometric pressure were observed for each weighing. The air in the balance case was kept dry by means of calcium chloride, which was frequently changed. The weights used were some made by Westphal; their errors were carefully determined before the commencement of the experiments; one of the 10-gram weights was taken as a standard. All weighings were reduced to a vacuum standard by calculation from the specific gravities of the substances and weights involved;

the fractions of a gram were calculated as brass, and not as platinum. The following numbers were taken for the specific gravities:—

Brass	8.45 (specially determined)
Crystalline borax....	1.62
Fused borax	2.29 (specially determined)
Sodium chloride	2.16
Silver chloride	5.5

The specific gravity of the fused borax was determined by weighing it in air and then in chloroform, the density of which had been determined in the ordinary way by comparison with an equal volume of water. The specific gravity of the weights was determined by weighing the 50-gram weight in air and then in water. The usual method of weighing by vibrations was adopted.

Methods and Materials employed.

The methods we adopted to determine the atomic weight of boron were two in number:—

1. A preliminary redetermination of the water of crystallisation in borax.

2. Conversion of anhydrous sodium borate into sodium chloride by distillation of vitreous borax with hydrochloric acid and methyl alcohol, and weighing the sodium chloride produced.

The materials used consisted of pure borax, pure hydrochloric acid, and pure methyl alcohol.

Borax.—This was made by gradually adding to a solution of pure soda in hot water, contained in a platinum vessel, a slight excess of pure boric acid. The boric acid had been previously tested for sulphuric acid, and was found to be entirely free from it, and it volatilised with alcohol, leaving no residue. The solution of borax was filtered and allowed to crystallise. The mother liquor was removed and the crystals washed and drained by means of the water-pump, then redissolved in water, kept hot on a water-bath for some time, and left to crystallise; the crystals obtained were powdered, washed, and drained by the pump. This process was repeated; the powdered crystals were washed about 10 times with cold water, drained by the pump, then pressed in a filter-press, and left to dry in the air, the possibility of dust gaining access to them being carefully avoided. The borax was kept in a linen bag in order to test for efflorescence.

Pure Hydrochloric acid.—This was prepared by passing gaseous hydrogen chloride into water; the gaseous hydrogen chloride was obtained by boiling pure concentrated hydrochloric acid in a retort, with the neck inclined upwards so that no liquid could pass over, and collecting the gas given off in water. On evaporation, 50 c.c. left a

scarcely visible and quite unweighable residue. Since not more than 25 c.c. at the most would be required in the experiments, it was thought that the weight of this residue might be neglected.

Methyl alcohol.—A specimen of the alcohol, free from acetone, was redistilled, and, on evaporation, left no residue.

Method I.—Determination of the Water of Crystallisation in Borax,
 $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.

A weighed quantity of borax was placed in a platinum dish, and dried in an air-bath at a temperature of 95–98° for some time, till no more bubbles were observed. The temperature was then gradually raised to about 350°; the borax intumesced considerably, and in some cases loss occurred by spirting; the platinum dish was then removed from the air-bath, heated over a blow-pipe till the borax fused, allowed to cool, and weighed. In one or two cases, fuming was observed as if decomposition of the borax were taking place, but these were not included amongst the experiments from which the atomic weight was calculated.

The borax was exposed to the air on November 23; the date of each experiment is given in Table I, so that the time of exposure is known; the weather was more or less damp all the time, so that much efflorescence did not occur; but when the weather is dry, efflorescence takes place fairly quickly. Some borax was exposed for a fortnight in May during dry weather; an analysis gave 46·3027 per cent. of water instead of 47·10. Additional evidence that this method is inapplicable to the determination of the atomic weight of boron is given by the loss of water which borax undergoes when dried over sulphuric acid. Some ordinary recrystallised borax was placed in a desiccator over sulphuric acid, and portions analysed from time to time. The borax, on January 26, lost (a) 47·08 and (b) 47·05 per cent. before being placed in the desiccator. On February 2, the loss was 47·00 per cent.; on February 18, it decreased to 44·39 per cent.; on March 31, it was 35·75 per cent.; and on July 8, only 20·73 per cent.; showing that the borax had again given up a good deal of its water.

Two observations were made of the action on borax of prolonged heating over a Bunsen burner, but the weight remained unaltered.

Weight of crucible and borax fused over a bunsen..	6·4980
1. Weight of crucible and borax fused over a bunsen, and heated to bright redness for half an hour ...	6·4980
2. Weight of crucible and fused borax.....	10·0247
Weight of crucible and fused borax heated to bright redness for half an hour.....	10·0247

TABLE I.

Date.	Expt. No.	Weight of crystalline borax.	Weight of fused borax.	Water lost per cent.	Atomic weight of boron.
Dec. 1 . . .	3	10·3581602	5·4784357	47·1099	11·04
„ 4 . . .	5	5·3440080	2·8246677	47·1433	10·97
„ 4 . . .	6	4·9962580	2·6378934	47·2026	10·85
„ 7 . . .	7	5·7000256	3·0101127	47·1912	10·87
„ 8 . . .	9	5·3142725	2·8065646	47·1882	10·88
„ 11 . . .	11	4·9971924	2·6392016	47·1865	10·885
„ 11 . . .	12	5·2366921	2·7674672	47·1524	10·955
	Aggregate	41·9466088	22·1631808	47·1633	10·93

Mean atomic weight of boron, 10·921.

Probable error, $\pm 0\cdot010$.*Method II.—Distillation with Hydrochloric acid and Methyl alcohol.*

This method is one which has been successfully employed in the quantitative estimation of boric acid; it is, in fact, a modification of that employed by Schweizer for the estimation of borax. He dissolved a known weight of borax in water, added hydrochloric acid in excess, and evaporated on a water-bath; more hydrochloric acid was added towards the end of the operation, and the residue kept on the water-bath till no more hydrogen chloride came off. The chlorine in the residue was then estimated.

Our plan consisted in dissolving a known quantity of anhydrous borax in a small amount of water; adding methyl alcohol and an excess of hydrochloric acid, then distilling on a water-bath with methyl alcohol till boric acid could not be detected in the distillate with the flame test; when this point was reached, a little more hydrochloric acid was added, and distillation was repeated four or five times after any boric acid had been detected; the last time of distilling, as much of the liquid as possible was driven over. The flask was then put in an air-bath, and, after being heated for some hours at $90\text{--}110^\circ$ in a constant slow current of air, the temperature was raised to about 350° for two or three hours, as the sodium chloride could not be thoroughly dried at the lower temperature; after cooling and standing for some time in the balance case, the flask was weighed. The amount of sodium chloride formed from the borax was thus obtained; the sodium present in it was calculated; from this amount of sodium, the borax corresponding to two atomic proportions, or 46·1 grams of sodium was found; this number, less Na_2O_7 , gave B_4 , and hence the atomic weight of boron.

In the first series of experiments, a flask of ordinary soft glass was used of about 100 c.c. capacity; it was furnished with a side tube like an ordinary distilling flask, but the neck was fitted with a hollow ground glass stopper, into which a tube was sealed, which passed down into the flask, and the upper part of which was furnished with a stop-cock, so that alcohol could be added without opening the flask; it also served for the passage of a current of air during drying. The results obtained were not very concordant, for the flask was attacked during the distillation; on dissolving the salt in water, a considerable residue of silica was left, so oxygen in the alkali had been replaced by chlorine, and the weight of the flask increased. However, the mean of these results is not very far from that obtained in the next series.

The two probable sources of error, besides action on the flask, are an incomplete conversion of sodium borate into sodium chloride, and possible loss by spurling. It was thought that the former might be avoided by the use of an excess of hydrochloric acid, and that spurling would be hindered by the shape of the flask. In one experiment, a bulb plugged with glass wool was attached to the distilling tube, so that any salt carried over as spray would be stopped; when the distillation was finished, the bulb was washed out with water several times, the solution filtered and evaporated to dryness; no residue was left, proving that no sodium chloride had been carried over with the alcohol vapour.

The results of these experiments are given in Table II.

TABLE II.—*Distillation Series I.*

Expt. No.	Weight of $\text{Na}_2\text{B}_4\text{O}_7$.	Weight of NaCl .	Atomic weight of boron.
14	4.7684431	2.7597665	11.015
15	5.2740318	3.0578213	10.925
16	3.2344088	1.8727203	10.992
17	4.0861923	2.3713122	10.879
18	3.4970297	2.0265645	10.949
Aggregate	20.8601057	12.0881848	10.951

Mean atomic weight of boron, 10.952.

Probable error, ± 0.010 .

To avoid any error caused by the attack of the soft glass flask, we then tried a flask of pure silver, but it was attacked to a considerable extent by the hydrochloric acid, for, on washing out the flask, a good deal of silver chloride was found, and the weight of the supposed

pure salt was considerably augmented. To convert the loss of weight of the flask into silver chloride, and deduct this from the weight found for the salt, did not seem accurate enough for an atomic weight determination, especially as in the second experiment the substance insoluble in water was more like silver oxide than chloride in appearance. The use of the silver flask was therefore abandoned.

The second series of distillations were conducted in flasks made of combustion tubing. One of the flasks was boiled with hydrochloric acid for some hours, and underwent no alteration in weight; it was, however, found that during distillation with hydrochloric acid and alcohol, the flasks were slightly attacked, for on extracting the sodium chloride with water, a slight insoluble residue of silica was left. In one case this insoluble residue was collected on a filter, dried, ignited, and weighed; the weight corresponded within 0.15 milligram to the loss in weight of the flask.

The flasks were of about 100 c.c. capacity, and with rather long necks; owing to the difficulty in working combustion tubing, the flasks were not provided with the ordinary side tubes for distilling, but a cap of wider tubing fitted over the neck of the flask, and this had a narrow tube attached. Loss of sodium chloride by spurt-ing was guarded against by keeping the flask inclined, so that the spray was projected against the upper side of the flask, and only the vapour passed up the neck. The rate of ebullition was regulated, so that no bumping occurred; it was found that the boric acid volatilised more readily when the distillation proceeded with fair rapidity. The method of procedure was exactly the same as in the first series, distillation being repeated four times after the last detection of boric acid, and the drying conducted as before. In order to check the results, the salt, after weighing, was dissolved in water and the flask washed out till no trace of chloride could be detected in the liquid; the solution was filtered to remove the small insoluble residue, and an estimation of the chlorine made in the ordinary way with silver nitrate. The silver chloride was collected on a Gooch's filter and dried in an air-bath, the temperature of which was ultimately raised to 200°. In every case the results obtained were a little low for pure salt, but agreed very closely among themselves. The solubility of silver chloride in water is so slight that it would hardly account for the discrepancy, and if the error is due to the presence of sodium borate which has not been transformed into salt, it seems remarkable that the results should be so concordant.

If the atomic weight of boron is calculated from the chlorine determination, it becomes rather higher, with a mean of 11.052.

When silver is used in atomic weight determinations, the greatest care is taken to obtain it absolutely pure; we employed the ordinary

silver nitrate supplied as "pure," so it is probable that the atomic weight determined from the distillations is more correct.

Whichever is regarded as the more probable determination, it is higher than that obtained by Abrahall, and much nearer to an integer.

The results of these distillations are given in Table III; the silver determinations are inserted for the sake of completeness. The theoretical percentage of chlorine in sodium chloride is 60.598, taking Clarke's atomic weights.

TABLE III.—*Distillation Series II.*

Expt. No.	Weight of fused borax, $\text{Na}_2\text{B}_4\text{O}_7$	Weight of sodium chloride, NaCl .	Atomic weight of boron.
22	5.3118075	3.0761181	10.983
23	4.7805583	2.7700458	10.955
24	4.9907395	2.8929844	10.936
25	4.7231225	2.7360411	10.968
26	3.3137921	1.9187258	10.992
Aggregate	23.1200199	13.3939152	10.965

Mean atomic weight of boron, 10.966.

Probable error, ± 0.005 .

Expt. No.	Weight of silver chloride, AgCl .	Chlorine per cent. in sodium chloride.	Atomic weight of boron from chlorine.
22	7.525869	60.493	11.071
23	6.7794186	60.515	11.024
22	7.0804317	60.516	11.003
25	6.6960242	60.514	11.039
26	4.6931271	60.479	11.091
Aggregate	32.7748706	60.505	11.084

Mean atomic weight of boron, 11.052.

Probable error, ± 0.010 .

The probable sources of error in these experiments are the following:—

i. *Impurities in the Borax.*—It is not likely that any impurity was present, for pure soda made from sodium was used, and pure boric acid, which was entirely volatile with alcohol, and gave no reaction for sulphuric acid. If any decomposition took place on fusing, so that the sodium borate contained a small amount of sodium oxide,

the weight of the supposed pure sodium borate would be too great, and therefore the atomic weight found would be too high.

ii. *Attack of the Glass Flask on Boiling with Hydrochloric acid and Alcohol.*—This occurred to some extent in the series of experiments performed in the soft glass flask, but the hard glass was acted on to a very small extent. The presence of silica in the liquid, when the flask was washed out with water after the sodium chloride had been weighed, points to the displacement of oxygen by chlorine in sodium silicate, silica and sodium chloride being obtained. There would thus be an increase in weight in the flask, and the weight of the salt would be too great, being found by deducting the original weight of the flask; this would cause the atomic weight to be too low.

iii. *Loss by Spurting.*—It is not likely that this took place, because of the precautions observed, but if loss did occur, it would make the atomic weight too high.

iv. *Incomplete Conversion of the Sodium Borate into Sodium Chloride.*—Since the percentage of chlorine in the sodium chloride deduced from the determination of the chlorine by means of silver nitrate was rather low, it is not improbable that the conversion was not quite complete. The supposed pure sodium chloride would weigh rather too much, and the atomic weight found would be too low. In the case of the aggregate results in Table III, if the salt is determined from the weight of silver chloride, it is 13.3733 grams, that is, a less weight by 0.0206 gram than that obtained from direct weighing of the sodium chloride. If this is regarded as the weight of undecomposed borax, and subtracted from the total weight of borax taken, it gives the amount of borax which takes part in the reaction; the atomic weight thus becomes $B = 10.997$.

From these results it appears that the atomic weight of boron is very nearly 11, and not far from that obtained in the older determinations, but higher than that obtained by Mr. Abrahall.

The silver chloride which we obtained from the salt was soluble in ammonia, and did not give a blue solution, so no copper could have been present as an impurity.

Boron nitride, BN , is a definite, very stable substance, and we tried, but without success, to use it in this atomic weight determination. An intimate mixture of pure crystallised boric acid and pure ammonium chloride was heated to bright redness in a platinum crucible, but some boric acid volatilised with the water given off in the reaction, so that this method did not give a quantitative yield of boron nitride. Another attempt was made with previously fused boric anhydride and ammonium chloride, but probably decomposition of part of the boron nitride formed was caused by the water produced during the reaction, for loss of weight took place further than

would give the atomic weight of boron anywhere near 11. A trial was made by heating the mixture over a Bunsen flame, but the temperature was insufficient to do more than volatilise the ammonium chloride, and fuse the boric anhydride. It appears to be an extremely difficult matter to obtain pure boron nitride; it is nearly always rendered impure by boric acid, which clings to it most tenaciously.

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