XIV.—*The Density of Boric Oxide Glass and the Suspected Variation in the Atomic Weight of Boron.*

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Through the courtesy of Messrs. Borax Consolidated, Ltd., the authors, in 1922, were in possession of several parcels of boron minerals obtained from various parts of the world and containing a high percentage of boron. At that time an attempt was made to compare the atomic weights of the several specimens of boron contained in these minerals by preparing from each a specimen of boric acid, purifying these specimens by rigorous fractional crystallisation, and determining the density at 25·00° ± 0·02° of their aqueous solutions saturated at that temperature. The accuracy of the results as measured by their reproducibility fell short, however, of that necessary to give trustworthy evidence of any difference in atomic weight and this method of attack was abandoned.

Thereafter three of the samples of boron were used for determinations of the atomic weight by measurement of the ratio $BCl_3 : 3Ag$ which have already been reported (J., 1925, **127**, 700). These determinations gave evidence of an appreciable variation in atomic weight among the three samples. Therefore, as sufficient of all the original mineral samples was still available, a fresh attempt was made to obtain a comparative estimate of the atomic weights by determining the densities of samples of a solid boron compound prepared from the several sources. Of the available compounds, boric oxide glass appeared to be the most suitable; boric acid is easily prepared from the minerals, its low solubility in cold water renders its recrystallisation an excellent method of purification and it readily dehydrates to yield boric oxide glass, which, because of its chemical stability and transparent glassy character, seemed to be especially well suited to precise density determinations.

Although much attention has been given to the improvement of the specific gravity bottle (see, *e.g.*, Berkeley, J., 1907, **90**, 56; Baxter, *J. Amer. Chem. Soc.*, 1908, **30**, 46; Johnson and Adams, *ibid.*, 1912, **34**, 563), it is difficult to attain high accuracy in the determination of the density of solids by displacement methods. Moreover, as boric oxide is extremely hygroscopic, being in fact coated with an opalescent film of hydrated oxide in less than one minute when exposed to air of ordinary humidity, it is clear that the use of any form of specific gravity bottle for the determination of its density is attended by very serious difficulty. Therefore it was decided to use a modification of the flotation method suggested by Andreae (*Z. physikal. Chem.*, 1911, **76**, 491). Beads of pure boric oxide glass prepared from each of six sources, with all precautions to exclude traces of moisture, were sealed up in tubes containing the same mixture of dry, inert organic liquids of suitable density; then careful observations were made of the *temperature* of flotation of the beads of each sample. Separate determinations of the density and thermal expansion of the liquid mixture enabled the actual densities of the boric oxide samples to be calculated. Thence, using the ascertained atomic weight of the boron in one sample as a standard, it was possible, assuming identity of atomic volume for all specimens of boron, to calculate the atomic weights of the specimens of boron in the remaining samples.

EXPERIMENTAL.

Preparation of Beads of Pure Anhydrous Boric Oxide.—The sources of the various samples were:

No. 1. Calcined borate of lime; Ascotan, Chile.
No. 2. Calcined colemanite; Death Valley, California, U.S.A.
No. 3. Borate of lime; the Argentine.
No. 4. Borate of lime; Peru.
No. 5. Boracite; Sultan Tchair, Asia Minor.
No. 6. Crude boric acid; Volterra, Italy.

Samples 1 to 5 were separately treated as follows: 200 g. of mineral were dissolved as far as possible in hot 10% hydrochloric acid, the solution was filtered hot, cooled quickly, and the precipitated boric acid was removed by filtration. The acid was twice recrystallised from pure water, the product was fused in platinum and then dissolved in pure hot water and allowed to crystallise. From this stage all the samples of boric acid, including No. 6, were twice recrystallised from pure water and each batch of crystals was tested for purity.

Owing, presumably, to the insolubility of calcium borate and the comparative insensitivity of available tests for calcium, no trace of that metal could be detected in the boric acid even at an early stage of the purification, but sulphate and chloride were then present in detectable amounts. Therefore the progress of purification in the later crystallisations was followed by tests for sulphate and chloride, and the apparent absence of these radicals in the final main crops of boric acid and in the mother-liquors whence these had come was taken as an indication of high general purity. The purified boric acid was stored in clean stoppered bottles, capped to exclude dust.

In the preparation of beads 10 g. of each sample were fused for 4—5 hours in a *suitable* covered platinum crucible heated at about 900° in an electric muffle furnace. The term *suitable* is stressed because it was only after several trials that a platinum crucible was found from which iron was not leached by the melt. Even after this drastic treatment, boric oxide still contains water, presumably because the high viscosity of the melt hinders its escape, and in order to dehydrate the material completely and prepare suitable individual samples for flotation, the crucible was again heated over a Méker burner and a quantity of the fused oxide was collected on a platinum wire. This was heated in a hot bunsen flame for 1 minute and if it then showed no sign of bubbles—a clear indication of the complete absence of water—it was allowed to drop from the wire directly into a clean cold platinum basin, which had been previously heated to redness and then rested in a desiccator over phosphoric oxide, the lid of the desiccator being raised for the minimum time. When bubbles appeared in a bead, the material was rejected, as it was found that such beads could be almost completely volatilised before losing their vesicular structure. The beads were about 3 mm. in diameter and from 30—35 were prepared from each sample. A number of test beads examined under the microscope were isotropic, contained no visible bubbles and, between crossed Nicols, appeared free from strain.

Preparation of the Flotation Liquid.—No single liquid of suitable chemical nature having the required density could be found, so a binary mixture was used. It appeared that the constituents of this mixture should be chemically stable and non-reactive, should be capable of being thoroughly dried by means of phosphoric oxide, should have densities slightly below and above 1·8, should have closely similar and preferably rather high boiling points and fairly low viscosities. The requirements of the case were met by a mixture of pentachloroethane (b. p. 161·7°, *D* 1·693) and trimethylene dibromide (b. p. 165·0°, *D* 1·987) containing 61·07% by volume of the former liquid. Both liquids were obtained from Messrs. British Drug Houses, Ltd.; and were further purified by fractional distillation, about 20% being rejected as head and tail fractions. The main fraction of pentachloroethane was collected between 160° and 162·5° at 762·6 mm. and that of trimethylene dibromide between 164·0° and 167·0° at 762·6 mm.

FIG. 1.

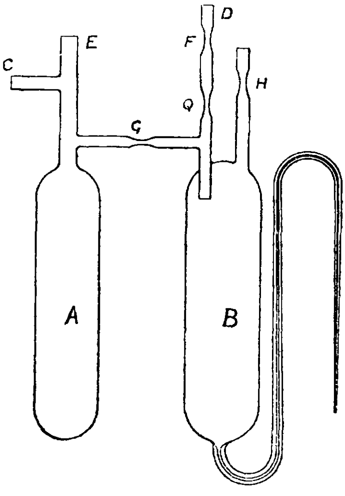


FIG. 2.

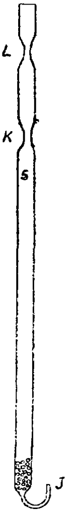
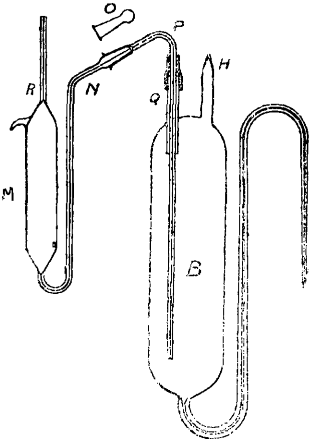


FIG. 3.



About 120 c.c. of the mixture were left in contact with phosphoric oxide for 24 hours. Slight decomposition and darkening occurred, probably owing to slight conversion of trimethylene dibromide into propylene dibromide (b. p. 141·7°, *D* 1·9), but the method of experiment ensured that any change in the density or volatility of the mixture thus produced would have no effect on the density found for boric oxide.

The apparatus used for the final purification and preservation of the flotation mixture is shown in Fig. 1. Both it and the other apparatus to be described later were constructed throughout of "Durosil" glass and before use were soaked in a solution of chromic acid in strong nitric acid, washed very thoroughly with pure water, dried in an air-oven at 150°, and finally swept out for some time with a slow stream of air which had been cleaned by bubbling through concentrated aqueous potash and dried by passage over solid caustic potash and phosphoric oxide. The tubes at H and I being temporarily sealed by fusion, a stream of dry air was passed in at C and out through a phosphoric oxide guard-tube on D, and the liquid mixture was introduced through E into the vessel A : tubes E and C were then sealed. A was cooled with ice and the apparatus was evacuated by a Gaede pump through D, which was finally sealed off at the constriction F. At this stage the liquid was almost completely distilled from A to B. Then both A and B were cooled with ice, dry air was slowly admitted at C, and the vessel B was sealed off from A at G. The reason for thus admitting air was to displace the vapour of the organic liquids from the connecting tube before sealing off : in this way perfectly clean seals were obtained, whereas the vapour, if present, carbonises when heated to redness. The vessel B was stored in a dark place until required.

Filling of the Flotation Tubes.—These tubes, of the form shown in Fig 2, were constructed of very thin-walled Durosil tubing of about 8 mm. bore, had a fine bent capillary at J, and were slightly constricted at L and K. The length of the tube between K and J was about 30 cm. Each tube bore an etched number corresponding with the sample of boric oxide it was to contain, and was charged with beads as follows : While dry air was passed through J up the perfectly clean and dry tube, beads, from 30—35 in number, of one sample of boric oxide were quickly removed from the phosphoric oxide desiccator and poured into this tube : the tube was then immediately sealed off first at L and then at J.

The procedure for filling the tubes with liquid was necessarily elaborate, but worked without a hitch in practice. A large aspirator bottle, containing a quantity of loose phosphoric oxide and air under slight pressure, was connected to the sealed tip of F (previously scratched with a file) by pressure tubing, through a train consisting of a tap, a phosphoric oxide guard-tube and a T-piece opening to the atmosphere by means of a tap and phosphoric oxide guard-tube on the side limb. The apparatus having been very thoroughly dried, pressure was raised in the aspirator and the whole was allowed to stand for over an hour to ensure adequate drying of the additional air. Thereafter the tip F was broken inside the rubber tube and the fine delivery tube I was also opened near the tip and at once inserted in a guard-tube carrying a current of dry air. Then each flotation tube in turn was cracked just below L by means of a sharp file and a hot rod, the top was lifted off, a fine bent tube delivering a current of dry air was passed down below the constriction K, and then the flotation tube was slipped quickly over the jet I of the reservoir B, from which the guard-tube had been that instant removed. By admitting air from the aspirator, liquid was forced over from B until the flotation tube was filled to a depth of about 20 cm. The flow of liquid was stopped by shutting off B from the aspirator and releasing the pressure in B by opening to the air the guarded tap in the connecting train. Then the flotation tube was withdrawn from I (and replaced immediately by the guard-tube), the fine tube delivering air was lifted just above the constriction K, and the flotation tube was sealed with the blow-pipe at that point.

After the drill had been mastered by practice runs on blank apparatus, this procedure occupied much less time than it takes to describe. In the final experiments, the time required to fill a tube averaged four minutes, and no one tube was open for more than $4\frac{1}{2}$ minutes.

Determination of the Density and Thermal Expansion of the Liquid.—For this purpose a special pyknometer of the form shown at M (Fig. 3) and holding about 10 c.c. was used. It had at N a taper ground carefully to fit both the cap, O, and the bent extension tube, P, and at R a fine engraved reference mark. Both tubes of the pyknometer were of very fine bore. It was weighed against a precisely similar pyknometer as tare, on a balance having a sensitivity of 20 scale divisions per mg., by means of a set of weights carefully calibrated in air for atomic weight work.

Five determinations of the weight of the pyknometer empty, made after various washings, fillings and immersions in the thermostat bath, gave concordant results, and thus afforded evidence that the error of weighing was probably insignificant. The weights of the pyknometer filled with pure water at 17·00° and 19·45° were determined in triplicate and thus, by means of the known specific volume of water, the absolute volume of the pyknometer at these temperatures was ascertained.

In filling the pyknometer with the flotation liquid the reservoir B (Fig. 3) was opened at Q, the carefully dried extension tube P (closed at the ground end by means of a rubber cap) was slipped in, and an air-tight joint made by sliding the wired-on rubber sleeve over the tube P. The reservoir was opened through a phosphoric oxide guard-tube at H. Both reservoir and pyknometer were then clamped to a retort stand and immersed over the barrels in the water of the thermostat tank maintained at 17·00° ± 0·02°. After 20 minutes, the retort stand was lifted from the bath, the pyknometer was connected by the ground joint N to the reservoir and filled with liquid forced over by admitting dry air through H. Then the pyknometer was disconnected and P was closed with its rubber cap.

These operations having been carried out very quickly, the stand and vessels were returned to the thermostat and held at 17·00° for a further 30 minutes. Then the liquid level in the pyknometer was adjusted by drawing off the excess with a piece of pure filter-paper, and the pyknometer was stoppered, removed from the bath, dried carefully, and weighed with all due precautions. It was then replaced in the thermostat, maintained at 19·45° ± 0·02° for 40 minutes, the liquid level was again adjusted, and the pyknometer was stoppered, dried, and weighed as before.

These determinations gave the data necessary to ascertain with the requisite precision the absolute density of the liquid at two temperatures, comprising between them the range of flotation temperatures. The density at intermediate temperatures was obtained on the assumption, clearly justifiable for so short a temperature range, that the relation of density to temperature is linear, and was read from a large-scale graph.

Determination of Temperature of Flotation.—The six flotation tubes, together with an open-scale thermometer graduated in 0·1°, were mounted vertically by means of rubber bands on two horizontal rods clamped to a retort stand. The whole apparatus was then immersed in a copper tank, with plate glass sides, containing about 27 litres of water. The tank was fitted with a motor-driven paddle, and at about room temperature this arrangement proved to be sufficiently thermostatic for its purpose. In a preliminary test, the temperature was raised slowly from about 17° to about 19·5° by the addition of quantities of 100 c.c. of hot water at regular intervals, and the approximate temperatures of flotation of the several samples of beads were observed. The final observations were made in each tube separately, and the temperature at which the beads remained suspended was noted for each sample. In all cases one or two beads—never more—whilst of the same order of density, appeared to be slightly heavier than the rest and sank first. The movement of the next lot in order of density, usually upwards of 6 (which were followed down almost immediately by the main bulk), was therefore observed with the aid of a fixed telescope, and the bath temperature was carefully regulated until they were brought to rest midway in their fall through the liquid. These beads were maintained stationary in suspension for 30 minutes and the temperature was observed every 3 minutes : these temperature readings did not vary over a greater range than 0·02° and the mean value was taken as the flotation temperature.

As the beads floated for ½ hour at a substantially constant temperature, it is evident that they must have been in thermal equilibrium with the liquid. Any small defect in this respect would have a negligible effect on the results owing to the smallness of the thermal expansion of boric oxide glass. Samsoen (*Compt. rend.*, 1925, **181**, 354) has shown that up to 240° this has a value about 15×10^{-6}, whence a change of temperature of 0·1° (which is large in relation to the present measurements) changes the density of the glass by about one unit in the eighth decimal place.

Further, the prompt movement of the beads when the slightest perceptible change was made in the bath temperature showed that the flotation liquid within the tubes acquired the temperature of the bath with very little delay, probably within one minute. This is the more probable because other experiments in progress in these laboratories have shown that some 60—100 c.c. of liquid contained in a sealed tube 30 mm. in diameter with walls 1½ mm. thick, without agitation, requires only some 8—15 minutes to acquire within 0·01° the temperature of a water-bath in which it is wholly immersed.

Results.

The following values for the density of the liquid, relative to water at 4°, are each the mean of two concordant determinations :—

Temperature	17·00°	19·45°
Volume of pyknometer	9·7822 c.c.	9·7825 c.c.
Weight of liquid contained by pyknometer	17·5858 g.	17·5471 g.
Density of liquid	1·79773	1·79372

The table given below shows for each sample of boric oxide the flotation temperature, the corresponding density, the atomic weight calculated from the density, and, in the case of three samples, the atomic weight derived from determinations of the ratio $BCl_3 : 3Ag$ using boron trichloride prepared from the same original sample: In calculating the atomic weight corresponding to the ascertained density, sample 5, derived from boracite from Sultan Tchair, Asia Minor, was taken as standard, with the atomic weight B = 10·818. Hence for any other sample, X, the atomic weight is found by :

$$\text{At. wt. of boron in X} = \tfrac{1}{2}\left(\frac{\text{Density of X} \times \text{Mol. wt. of standard } B_2O_3}{\text{Density of standard } B_2O_3} - 48\right).$$

Sample No.	Place of origin.	Flotation temp.	Density.	Relative atomic weight.	
				Calc. from density.	Determined from ratio $BCl_3 : 3Ag$.
2	California	17·36°	1·79711	10·847	10·841
6	Tuscany	18·15	1·79583	10·823	10·825
5	Asia Minor	18·30	1·79558	10·818 (standard)	10·818
1	Chile	18·30	1·79558	10·818	
3	Argentine	18·65	1·79501	10·806	
4	Peru	19·25	1·79404	10·788*	

* The beads of this sample showed a considerably greater variation in density among themselves than was observed in the case of the other samples Hence the authors attach less weight to this figure than to the data for samples 1—5 inclusive.

Discussion of Results.

The method of determining densities here described may clearly be made to yield extremely precise results and is applicable to a great variety of solids, provided that a suitable flotation liquid can be obtained. The values recorded show that the mean density of pure fused boric oxide is 1·7952 and that the value 1·88 commonly used is considerably in error.

The estimated maximum error in the determination of the specific gravity of the flotation liquid is ± 0·00008 : the actual error is probably rather less at temperatures intermediate between 17·00° and 19·45°. Owing to the means adopted to ensure that all the flotation tubes were filled at one time from the same well-mixed bulk of liquid, the *relative* values of the specific gravity deduced from the flotation temperatures are probably uncertain only in so far as those temperatures are uncertain. It is unjustifiable to attempt to report in detail the very numerous and detailed records of the observations of flotation temperatures, but they have been subjected to the most critical examination by the three authors working independently and the utmost difference of opinion thus elicited in their interpretation would not affect by one unit the third decimal of the atomic weight in any case. Hence it seems probable that the relative densities have an error less than 1 part in 10,000 parts, and that the maximum error in the relative values of the atomic weight does not exceed four or five units in the third decimal.

Admitting the view here expressed as to the precision of these results, the observed differences among them require explanation. The authors believe that the samples of boric oxide are very pure and, moreover, that the uniformity so carefully observed in their purification and subsequent treatment should have ensured that any impurity, for example, a possible trace of water, which they may have retained can have had little influence on the *relative* values found for their densities. Hence the observed differences are attributed to a variation in the atomic weight of one of the elements present and as there exists no evidence that such variation is possible in the case of oxygen, it is assumed to occur in the atomic weight of boron. The good agreement in three cases between the relative atomic weights deduced from the density values and found by the determination of the ratio $BCl_3 : 3Ag$ (Briscoe and Robinson, J., 1925, **127**, 696) can scarcely be accidental, and the authors believe that the present work confirms the conclusions drawn in the paper cited.

If these atomic weight values are correct, it is remarkable that the atomic weights of boron from the Argentine and Peru are very appreciably lower than any values hitherto recorded.

Evidently a determination of the boron halide : silver ratio for material from these sources would constitute a valuable check on the present results and conclusions, and the authors have considered undertaking this investigation. It appears to them, however, that any further work they might do on the atomic weight of boron can add but little to the value of the evidence they have already advanced, and that they should now leave it to other chemists to confirm or refute the conclusion, drawn from that evidence, that boron, like lead, has an atomic weight varying with its source. It is much to be hoped that this further investigation will be undertaken.

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