CCCXLIX.—*The Density of Boric Oxide Glass and the Atomic Weight of Boron.*

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In an important paper on this subject, Briscoe, Robinson, and Stephenson (J., 1926, 70) were concerned, not with the absolute atomic weight of boron, but with the relative values for the element present in boron minerals obtained from various terrestrial sources, and in the discussion of the results they were inclined to think that the maintenance by them of the same conditions of preparation of the boric oxide glass samples would ensure a valid comparison of density values even supposing some slight error might be present in the absolute values due to the inclusion of minute traces of moisture.

Of the six preparations of boric oxide, obtained from different sources, the densities ranged between 1·79711 (at 17·36°) and 1·79404 (at 19·25°), corresponding to extreme variations in calculated atomic weights for boron of 10·847 and 10·788. These differences in densities are substantial, being no less than three units in the third place of decimals. Differences in the temperature of determination in no way account for them: as the authors themselves indicate, a temperature change of 0·1° should only modify the density by one unit in the eighth decimal place. Consequently, the authors were led, in conjunction with certain other evidence, to conclude "that boron, like lead, has an atomic weight varying with its source."

In reopening this subject for discussion, we have no observations to make on the evidence previously obtained by Briscoe and Robinson (J., 1925, **127**, 696) on the basis of their determination of the ratio BCl_3 : Ag, but we are concerned with the density determinations on boric oxide glass and with their interpretation; for when reading the paper of Briscoe, Robinson, and Stephenson on its publication, doubt immediately occurred to one of us of the adequacy of the tests for strain in the beads of fused boric oxide. The authors stated: "A number of test beads examined . . . between crossed Nicols, appeared free from strain." It is by no means easy, however, to detect in such a way strain existing in small spherical objects, and the authors might well have been misled. Moreover, the magnitude of the change brought about in the numerical values of physical properties of glasses due to the existence of stresses is not fully realised except by workers on the vitreous state. Pure boric oxide glass and glasses containing boric oxide are particularly susceptible to modification of physical properties according to the rate at which the specimens have been cooled.

Whilst the rapid chilling which the beads of fused boric oxide underwent as the result of dropping small quantities of the molten material into a cold platinum basin made us feel considerable doubt about the beads being strain-free, the very fair concordance between the results for the samples prepared from six different sources at first disarmed criticism. At the time of publication we were engaged in the study of the vitreous system boric oxide–silica, and later we directed our attention to the densities of preparations in this system. Our first determinations on samples prepared from slightly impure boric oxide gave $d_{4^\circ}^{25^\circ}$ 1·843, a value much higher than those of Briscoe, Robinson, and Stephenson. It seemed desirable, therefore, that we should investigate carefully this discrepancy. The account which follows is a brief summary of the work undertaken, the stages enumerated below, however, not necessarily appearing in the sequence in which they were investigated. The several factors considered as possible to account for the discrepancy were five in number.

1. *The Influence of Purity of the Sample.*—The boric acid utilised by us as the source of boric oxide in the earlier experiments was B.P. material containing total impurity of only 0·17%, equivalent to approximately 0·31% in the boric oxide prepared from it by fusion at 1400°. The densities obtained for a well-annealed boric oxide glass from material of the purity stated lay between 1·843 and 1·845 in various determinations.

The same boric acid when recrystallised once from 10% hydrochloric acid and three times from distilled water was found by repeated evaporation with pure methyl alcohol to contain impurity not exceeding 0·02%. The density of eight samples of well-annealed boric oxide glass prepared from this purified acid lay between 1·8435 and 1·8446.

2. *The Influence of the Method.*—Our earlier determinations were carried out by the displacement method, a specific gravity bottle being used, and by critical tests we were satisfied that the densities obtained by means of it were trustworthy to within 0·1%, a trifling error compared with the discrepancy between our values and those of Briscoe, Robinson, and Stephenson. To ensure still greater accuracy in the later stages of the investigation, we used a flotation

method with pentachloroethane and trimethylene dibromide, liquids which had been found suitable by the above authors. The mean of four determinations on well-annealed boric oxide samples in the case of the specific gravity bottle method was 1·8444, and from the flotation method 1·8439.

3. *The Influence of a Trace of Moisture and of the Temperature of Preparation.*—Fused boric oxide is hygroscopic and readily absorbs moisture on its surface, becoming opalescent in the process. A bright bead of boric oxide was balanced in the flotation liquid and then exposed to the atmosphere for 90 minutes; after exposure, it floated on the surface, indicating a diminution in density due to absorption of moisture, which was also indicated visually by a distinct opalescent film.

Experience over several years in the preparation of fused boric oxide glass has indicated that the last traces of water are eliminated with difficulty on fusing boric acid, and a temperature of 900° is insufficient. It appeared to us quite possible that the temperature employed by Briscoe, Robinson, and Stephenson may not have been adequate, for their fusion was carried out in a covered platinum crucible for 4—5 hours at 900°, followed by heating over a Méker burner and a final heating in a Bunsen flame of beads gathered from the crucible by a loop of platinum wire, and it is probable that the maximum temperature attained cannot have exceeded 1000°. Our own samples were prepared by fusion in platinum at 1400°; but in order to test the effect of temperature, a few beads were prepared by fusing boric acid at 1000° for 4 hours and subsequently following the procedure of Briscoe, Robinson, and Stephenson. The lowest density values obtained by us in our series of measurements were with the beads prepared at 1000° [see (5) on p. 2657], and it seems quite likely, therefore, that a small amount of moisture is still retained even after fusion at that temperature.

4. *The Effect of Annealing.*—This factor proved, without doubt, to be the cause of the big discrepancy between our results and those of Briscoe, Robinson, and Stephenson. We had already made measurements of the thermal expansion of fused boric oxide over the whole range of temperature up to the softening point, and had, therefore, been able to deduce the cooling curve requisite for thorough annealing. In a series of measurements on unannealed specimens, obtained by dropping beads into a cold platinum dish, the densities were found to lie between 1·8008 and 1·8067.

The care which must be exercised in annealing glasses required for precise physical measurements is illustrated in the following table, which contains the data for several sets of specimens, one group of them having been cooled more rapidly than the other.

1. *Rate of Annealing.*

Temp.	345°	325°	300°	275°	240°	205°	160°
Time (hours), Curve I ...	0·5	1·5	2·5	3·5	4·5	5·5	6·5
,, ,, ,, II ...	0·5	2·5	4·5	6·5	8·5	10·5	12·5

2. *Densities by Flotation Method.*

Sample No.	Size of bead (mm.).	Rate of annealing.	Density.
5*a*	3·2 × 4·7 × 5·8	As Curve I	1·8423
5*b*	3·3 × 4·5 × 7·0	,, ,,	1·8423
6*a*	—	,, ,,	1·8418
6*b*	—	,, ,,	1·8414
7*a*	(2·2 × 2·8) (two beads) (2·1 × 2·7)	As Curve II	1·8442
7*b*	(3·2 × 5·3) (two beads) (4·7 × 9·8)	,, ,,	1·8437
8*a*	—	,, ,,	1·8440
8*b*	—	,, ,,	1·8435

When the beads were cooled between 345° and 160° during the comparatively long time of 6½ hours, the densities were still some 2 units in the third place lower than when 12½ hours were devoted to cooling over the same range.

5. *The Influence of Bead Size.*—This question of size is bound up with the question of rate of cooling. In experiments with the boric oxide prepared at about 1000°, the beads being unannealed, a density of 1·8017 was obtained for a bead weighing 0·070 g. and 1·7929 for a bead of 0·111 g.

The results of this investigation indicate, in the first place, that the true density of pure fused boric oxide glass at a temperature between 18° and 25° is not 1·7952, as stated by Briscoe, Robinson, and Stephenson, but is more accurately 1·844 (the mean value of the results by the specific gravity bottle method being 1·8444, and by the flotation method 1·8439). Further, the low figures obtained by these authors are mainly due to inadequate annealing of the specimens, and, probably in a minor degree, to the fusion of the boric oxide at about 1000° only. It is clear from results obtained in this Department that in themselves the variations obtained by these investigators in the density results of boric oxide glass from six different terrestrial sources cannot be used as evidence in favour of the view that the atomic weight of boron varies according to the source of the mineral which contains it.

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