

XLV.—*The Density of Boron Trichloride and the Suspected Variation in the Atomic Weight of Boron.*

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A TECHNIQUE for the determination and comparison of liquid densities with great precision by means of glass floats has recently been developed in this laboratory (Robinson and Smith, J., 1926, 1262) and applied to the problem of the constancy of the atomic weight of silicon derived from different sources. As the differences disclosed in this case did not exceed 0.005 unit, *i.e.*, 1 part in 5612, it seemed advisable to apply this method to boron, where a maximum difference of 0.023 unit, *i.e.*, 1 part in 540, was originally found by measuring the ratio $\text{BCl}_3 : 3\text{Ag}$ (Briscoe and Robinson, J., 1925, 127, 696) and subsequently confirmed by a measurement of the density of pure fused boric oxide glass prepared from the same sources (Briscoe, Robinson, and Stephenson, J., 1926, 70).

Outline of the Present Investigation.

In the last stage of the purification, the samples of boron trichloride (Briscoe and Robinson, *loc. cit.*) had been divided by fractional vacuum-distillation into three fractions, and the middle fraction had been used for analysis. In the present investigation, the remaining fractions of each sample were combined and purified by two further distillations in a vacuum, with the rejection of lighter and heavier fractions in each distillation, and the densities of the final main fractions were determined. In the case of two out of the three samples, the liquids forming the final main fractions were distilled fractionally on to and away from the floats, and the densities of the several runnings were thus obtained. From these data, the mean density of boron trichloride, its coefficient of thermal expansion, and the relative atomic weight of the samples of boron present in the various fractions were calculated.

Preparation of Boron Trichloride.

The original sources of the boron used in the three preparations of the trichloride were :

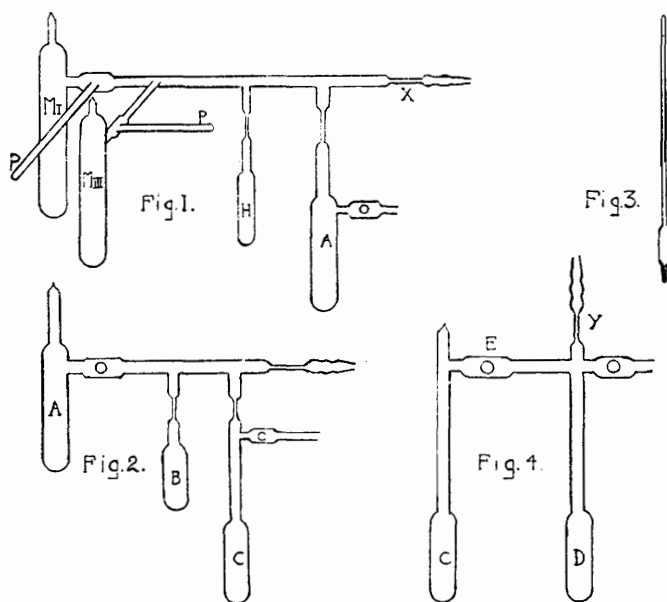
No. 1. Colemanite (calcined) from Death Valley, California, U.S.A.

No. 2. Crude boric acid from the neighbourhood of Volterra, Tuscany.

No. 3. Boracite from Sultan Tchair, Asia Minor.

Each sample, after receiving the uniform and rigorous purification

previously described, had been finally divided into five fractions designated T_6 , M_{III} , M_{II} , M_I , and H_5 (J., 1925, 127, 704, Fig. 1). T_6 and H_5 were small tail- and head-fractions of about 5–10 c.c., M_{II} was the main fraction for analysis, and M_{III} and M_I were tail- and head-fractions similar in size to M_{II} . M_{III} and M_I had been preserved in the original containers, having special joints which were now attached to a train (Fig. 1) carrying a head-fraction bulb, H, and a container with a special joint, A. M_{III} and M_I were arranged so that the plunger tubes, P, were at right angles to one another, thus enabling the capillary of either special joint to be



broken by moving the apparatus in the appropriate way. The apparatus was internally cleaned with the usual elaborate precautions, and after assembly was evacuated at X six times, being heated to 150° during each evacuation and thereafter slowly refilled with carefully dried air. Then it was sealed off with the McLeod gauge registering a pressure of 0.01 mm. The special joint of M_I was then broken and a head-fraction was distilled into H and sealed off. The rest of the contents of M_I was distilled into A. The special joint of M_{III} was then broken and its contents were distilled into A with the exception of a small tail-fraction; A was then removed by sealing off. This procedure was based on the assumption that, whatever impurity the material might contain, that in M_I would

probably have a lower b. p. and that in *M*III a higher b. p. than boron trichloride.

The vessel A was now attached to a second train (Fig. 2) which, after cleaning and drying as described above, was sealed off from the pump when the pressure had remained below 0.01 mm. for 30 minutes. B was thoroughly cooled with liquid air, the special joint of A was broken, and the small head-fraction which immediately collected in B was sealed off. C, which contained the two floats, was then cooled with liquid air and the material in A was very slowly and completely distilled at a temperature well below 0°. There were barely visible solid residues left in A from samples No. 2 (Tuscany) and No. 3 (Asia Minor), but there was a small although perceptibly greater residue in No. 1 (California). After the removal of C this residue, which was of the usual gummy character, was warmed and intumesced in the manner previously noted (Briscoe and Robinson, *loc. cit.*).

The Preparation and Standardisation of the Floats.

(The experimental work following is given in outline, and the references, unless otherwise stated, are to Robinson and Smith, J., 1926, 1262, where details may be found.)

The "Durosil" glass floats were prepared precisely as were those used in the determination of the density of silicon tetrachloride; they were rather shorter, as the volumes of the liquids available were less, and the densities of the individual floats of each series were closer together, the maximum difference being in the upper series 0.000194, and in the lower 0.000181.

Previous workers have given for the density of boron trichloride 1.35 at 17.5° (Wohler and Deville, *Compt. rend.*, 1857, 45, 888) and 1.43386 at 0°/4° (Ghira, *Z. physikal. Chem.*, 1894, 12, 768; *Gazzetta*, 1893, 23, i, 452). As these results were too divergent for the present purpose, a preliminary measurement was made. An all-glass hydrometer (Fig. 3) (suitably constructed from a piece of glass tubing of 0.8 cm. bore, with a solid sinker, a body 2 cm. long, and a fine stem 6 cm. long and 0.6 mm. in diameter) was calibrated in a series of bromotoluene-ethyl alcohol mixtures by measuring the length of exposed stem with a cathetometer. The densities of these mixtures were obtained with a Westphal balance. This little hydrometer, which had a range of 1.360—1.417 for a stem exposure of 2.390 cm. and gave readings to about 0.001, is detailed here because of its obvious convenience for such purposes as the present. A number of fractions of boron trichloride from the four-column still (Briscoe and Robinson, *loc. cit.*) were collected into a single vessel, sealed up over mercury for a fortnight, and then distilled in a

vacuum on to the hydrometer. A density of $1.350/11^\circ$ was indicated, which is in reasonable agreement with the value of Wohler and Deville.

An extensive series of liquids and mixtures was reviewed with regard to suitability for float calibration, *n*-propyl bromide (d $1.364/18^\circ$) being eventually selected. This liquid, from The British Drug Houses, Ltd., had d $1.346/19^\circ$, as measured by the Westphal balance. Two floats, with flotation-temperatures 10.14° and 15.20° , respectively, in *n*-propyl bromide, were tried out in the boron trichloride previously used for the hydrometer test by transferring the liquid *via* a special joint to another vessel containing the floats. The flotation-temperatures in boron trichloride were 7.45° and 11.19° , respectively; and it was therefore decided to work to flotation-temperatures of 10° and 12° , respectively (*i.e.*, below the b. p. at atmospheric pressure), these being equivalent, respectively, to 14° and 16° in *n*-propyl bromide. It was early noticed that the density of this liquid decreased with time (compare bromobenzene, *loc. cit.*), and the specimen used in the final calibration was therefore purified by one rough, followed by two careful, distillations with the rejection of head- and tail-fractions, the boiling points, taken every minute, having mean values $71.40^\circ/756.8$ mm. and $71.75^\circ/760.2$ mm. The standardisation of the floats was repeated with the once-, twice-, and thrice-distilled *n*-propyl bromide in the same apparatus (except that the float-lifter was of platinum, as nichrome was attacked), and with all the precautions previously described (*loc. cit.*), 161 flotation-temperatures being taken. As even the purified liquid tended to decrease in density with time, the final measurements for the six floats were completed within 8.5 hours of the third distillation, the flotation-vessel being then corked up. On the following day, the density of the liquid was determined at 16.857° and 20.873° , with the pycnometers and by the method previously described (*loc. cit.*), the results being 1.351288 and 1.344572 , respectively. Immediately afterwards two check flotation-temperatures were taken, the same liquid being used to establish the constancy of its density. These results are given in Table I which illustrates both the change in density of the *n*-propyl bromide and the increased permanency of its density with purification.

The Density of the Three Samples of Boron Trichloride at 11° .

Flotation-temperatures were obtained in exactly the manner described for silicon tetrachloride, except that, as the temperatures were constantly below that of the room, the bath was maintained in the required condition by a variable stream of ice-cold water from another tank. This arrangement was found to give excellent

TABLE I.

The Standardisation of the Floats in *n*-Propyl Bromide.

Float.	Flot.-temp. (C ₃ H ₇ Br once distilled).	Flot.-temp. (C ₃ H ₇ Br twice distilled).	Flot.-temp. (C ₃ H ₇ Br thrice distilled).	Density (g./c.c.).	Flot.-temp. (check after density determ.).
U	13.884°	16.922°	17.229°	1.350666	17.223°
Y	13.794	16.838	17.134	1.350825	
Z	13.819	16.819	17.121	1.350847	
V	15.809	18.909	19.223	1.347331	
W	15.839	18.787	19.106	1.347525	
X	15.849	18.802	19.123	1.347499	19.111

temperature regulation. About 130 flotation-temperatures were observed and those actually used differed by less than 0.010° for rising and falling temperatures. The floats showed markedly less tendency to become electrically charged than was the case in silicon tetrachloride (*loc. cit.*); the charges were most in evidence in the Asiatic sample, but even these were sufficiently reduced after two hours to allow flotation-temperatures to be taken. The charges were again positive in character (*loc. cit.*). Table II gives these results with the corresponding densities, the value 15×10^{-6} being used as the coefficient of cubical expansion of "Durosil" glass (Robinson and Smith, J., 1926, 3152). Table III gives the coefficients of cubical expansion calculated from the same data, together with the calculated probable error of the mean.

TABLE II.

The Density of Boron Trichloride.

Source.	Float.	F.-t. in BCl ₃ .	D at f.-t.	D of BCl ₃ at 11.000°.	Diff. from mean.
California	{ Y	10.351°	1.350963	1.349478	+0.000157
	{ X	11.800	1.347647		
Tuscany	{ U	10.326	1.350805	1.349273	-0.000048
	{ V	11.788	1.347482		
Asia Minor	{ Z	10.229	1.350987	1.349213	-0.000108
	{ W	11.666	1.347676		
Mean				1.349321	±0.000104

TABLE III.

The Coefficient of Thermal Expansion of Boron Trichloride.

Source.	Coeff. of exp.	Diff. from mean.
California	0.0016981	+0.0000004
Tuscany	0.0016868	-0.0000109
Asia Minor	0.0017073	+0.0000096
Mean	0.0016977	±0.0000070

Calculated probable error on mean, 0.0000040.

In Table IV are given the relative atomic weights of the boron present in the three samples, calculated by making the usual assump-

tions (*loc. cit.*) and taking Asiatic boron trichloride, d 1.349213 and atomic weight 10.818, as standard (the same standard is used throughout this paper). Table IV also includes for the sake of comparison the previous results of Briscoe and Robinson (*loc. cit.*) and of Briscoe, Robinson, and Stephenson (*loc. cit.*).

TABLE IV.

Source.	D .	At. wt. from	At. wt. from	At. wt. from
		D .	$\text{BCl}_3 : 3\text{Ag}$.	D of B_2O_3 .
California	1.349478	10.841	10.841	10.847
Tuscany	1.349273	10.823	10.823	10.825
Asia Minor	1.349213	10.818	10.818	10.818

For reasons dealt with more particularly below, the Californian and the Asiatic material underwent the further investigation next described. The flotation-vessels were severally attached to second containers constructed with long stems and special joints as illustrated (Fig. 4), to enable both vessels to be submerged to the same level in the bath. These were cleaned and dried with the usual precautions, being evacuated and refilled with dry air six times, with heating each time to about 150° , and were finally sealed off at Y when a pressure of 0.007 mm. had been registered for 30 minutes. After final check flotation-temperatures had been taken, the liquid in C was cooled with solid carbon dioxide and the special joint, E, was broken. This arrangement enabled the following operations to be performed: (a) distillation from C to D with determination of densities at intervals so long as there remained sufficient liquid to allow of the movement of one float; (b) pouring from C to D and distillation from D to C with density determinations at intervals as soon as there was sufficient liquid in C; (c) washing, by distilling a little liquid from the main bulk into the other vessel and then pouring back. Actually the material in C was distilled into D in stages, solid carbon dioxide being used as the cooling agent and bumping avoided by slightly cooling C; densities were taken at intervals. The residual liquid was then poured into D, and on three occasions small quantities were distilled into C and poured back into D. From D, which now held the whole of the liquid, it was distilled in stages on to the clean floats in C, densities being taken at intervals as soon as possible. These two sets of measurements were then repeated as a check. The numerous observations of flotation-temperatures in which two floats were used soon demonstrated that the temperature interval between the two floats was sufficiently constant to permit the use of one float only when this was convenient. Tables V and VI give the data for the Californian and the Asiatic boron trichloride, respectively.

TABLE V.
Californian Boron Trichloride.

Amount on floats.	Flotation-temperatures.		Observed temp.-interval.	Density.
	Float Y.	Float X.		
Total.	10-351°	11-800°	1-449°	1-349478
11/12 tail.	10-366	11-816	1-450	1-349514
10/12 "	10-381	11-829	1-448	1-349545
9/12 "	10-392	11-844	1-452	1-349575
8/12 "	10-406	11-854	1-448	1-349602
7/12 "		11-871		1-349639
			Mean 1-449	
2. Distilling from D to C.				
6/12 head.		11-738		1-349337
7/12 "		11-738		1-349337
8/12 "		11-741		1-349344
9/12 "		11-741		1-349344
10/12 "		11-744		1-349351
11/12 "		11-756		1-349378
Total (distilled).		11-796		1-349469
Total (washed).*	10-350	11-800	1-450	1-349478

TABLE VI.
Asiatic Boron Trichloride.

Amount on floats.	Flotation-temperatures.		Observed temp.-interval.	Density.
	Float Z.	Float W.		
Total.		11-670°		1-349212
13/15 tail.		11-683		1-349241
11/15 "		11-688		1-349252
9/15 "		11-699		1-349279
7/15 "	10-256°	11-701	1-445°	1-349281
5/15 "	10-259	11-707	1-448	1-349293
2. Distilling from D to C.				
7/17 head.	10-226	11-666	1-440	1-349213
10/17 "		11-673		1-349219
12/17 "	10-222	11-662	1-440	1-349207
14/17 "		11-670		1-349212
16/17 "	10-223	11-668	1-445	1-349213
Total (distilled).		11-679		1-349234
Total (washed).*		11-680		1-349235
			Mean 1-444	

* "Washed" indicates that a small amount of liquid had been poured back on to the residue and then poured forward again, and this operation repeated three times.

Discussion of Results.

The Density.—The relative error of the densities given above is probably less than ± 0.000002 , whilst the absolute value may, for reasons given elsewhere (*loc. cit.*), be as much as ± 0.00005 from the truth. The authors conclude that the values for the Californian,

Tuscan, and Asiatic materials are 1.349353, 1.349273, and 1.349211, respectively, giving a mean density of 1.349279 at $11.000^\circ \pm 0.005^\circ$ for an average sample of boron trichloride, these results being absolute and independent of the expansion of glass.

The Coefficients of Expansion.—The values given in Table VII for Californian and Asiatic materials are both derived from the mean of six intervals of temperature, whilst that for Tuscany boron is taken from Table III. The coefficients of expansion at 10° have a mean value of 0.0016954 with an error probably less than ± 0.000005 , and a calculated probable error of ± 0.0000030 . These results are absolute. Apparently this physical constant for boron trichloride has not been determined previously.

TABLE VII.

Source.	Mean temp.-interval.	Coeff. of exp.	Diff. from mean.
California	1.449	0.0016981	+0.0000027
Tuscany	1.462	0.0016868	-0.0000086
Asia Minor	1.444	0.0017014	+0.0000060
		Mean 0.0016954	± 0.0000058

Calculated probable error, 0.0000030.

The Relative Atomic Weights.—The relative atomic weights derived from a comparison of the density of the whole bulk of material from the three sources (see Table III) are in remarkable agreement with those of Briscoe and Robinson (*loc. cit.*), but as they were combinations of a head- and a tail-fraction taken before and after the portion analysed, with comparatively little subsequent rejection, it was clearly desirable to ascertain whether they were of uniform composition. Previous work upon the $\text{BCl}_3 : 3\text{Ag}$ ratio had indicated that a higher apparent atomic weight was to be expected in both the head- and the tail-fractions. The higher value for the latter was easily explained by assuming the presence of boric oxide or silicon tetrachloride, whereas the higher value for the head fraction, although it had been independently observed by Baxter and Scott (*Proc. Amer. Acad. Arts Sci.*, 1923, 59, 21), was difficult to account for, because the impurities to be anticipated here, *e.g.*, hydrogen chloride and chlorine, are such as would give a lower apparent atomic weight. From the data in Tables V and VI the density and corresponding apparent atomic weight of the separate fractions have been calculated and are given in Table VIII.

It is evident that in each case the extreme heads show a markedly lower density, and it may be presumed that this is related to the unexplained higher apparent atomic weight in the fractions mentioned above. On the other hand, the higher density in the case of the tail-fractions is very obvious, particularly in those of the Californian sample, where, as its effect is somewhat spread, *i.e.*, over the

TABLE VIII.

Source : California.			Source : Asia Minor.		
Head-fractn. Twelfth.	Density.	At. wt.	Head-fractn. Two-fifteenths.	Density.	At. wt.
1st	1.349082	10.807	1st	1.349024	10.802
2nd	1.349204	10.817	2nd	1.349181	10.815
3rd	1.349285	10.824	3rd	1.349131	10.811
4th	1.349359	10.831	4th	1.349272	10.823
5th	1.349343	10.829	5th	1.349251	10.821
6th			Seventeenth.		
7th	1.349337	10.829	8th, 9th, and 10th	1.349233	10.819
8th	1.349393	10.833	11th and 12th	1.349147	10.812
9th	1.349344	10.829	13th and 14th	1.349242	10.820
10th	1.349414	10.836	15th and 16th	1.349220	10.818
11th	1.349648	10.856	17th	1.349570	10.849
12th	1.350470	10.927			

10th, 11th, and 12th twelfths, it may be due to the presence of silicon tetrachloride as well as boric oxide. With the Asiatic material the effect is only noticeable in the last seventeenth and is probably accounted for entirely by the presence of boric oxide. Undoubtedly the liquid of Asiatic origin is the purer of the two samples in respect of less volatile materials, and this makes it difficult to select the figures which should be employed to arrive at the respective means. This difficulty has been avoided by arbitrarily taking means of (i) the first half, (ii) the first three-quarters, (iii) the middle half : these results are tabulated in Table IX.

TABLE IX.

	Californian.	Asiatic.	Difference.
(i)	10.823	10.813	0.010
(ii)	10.825	10.814	0.011
(iii)	10.830	10.817	0.013

These figures suggest that there is a real difference between the atomic weights of the two samples of boron, although this difference would seem to be less than that previously indicated by the $\text{BCl}_3 : 3\text{Ag}$ ratio. This discrepancy is explained by the traces of impurity disclosed in the Californian material in the course of the present investigation.

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