XCIX.—*A Redetermination of the Atomic Weight of Boron.*

By Henry Vincent Aird Briscoe and Percy Lucock Robinson.

In 1921, when the work here described was undertaken, the atomic weight of boron, usually taken as 11·0, was evidently uncertain to the extent of one or two units in the first decimal place. Consideration of all the available data for this atomic weight (Briscoe, Robinson, and Stephenson, this vol., p. 150) shows that the values published before 1922 range from B = 11·529 to B = 10·703 and give in mean approximately B = 10·95. Actually the uncertainty in this mean was even greater than appears from the figures, as it has been shown (*loc. cit.*) that there is reason to regard with grave suspicion all those determinations (14 out of a total of 24) dependent on the weighing of fused borax.

Therefore, in planning this investigation, we resolved to make a preliminary series of analyses to establish the method and then to carry out side by side three distinct and independent series of determinations, using samples of boron from widely separated, known sources, subjecting each sample before analysis to a rigorous purification, and ensuring particularly that all the samples had comparable treatment.

This method of attack was prompted also by another motive: the desire to inquire experimentally whether for boron the isotope-ratio is always and everywhere the same. Hitherto, in the great majority of atomic weight determinations, attention has been wholly concentrated on attaining great purity of the substance taken for analysis and the *origin* of that material has not been considered. Yet in the one case, that of lead, where materials of different known origin have been thoroughly investigated, results of the greatest interest and importance have accrued. These investigations, of course, arose from, and served to confirm, speculations as to the radio-active origin of lead, but it seems possible that an equally exhaustive examination of specimens of some of the lighter elements from different sources might throw some light upon the problem, at present quite obscure, of the origin and history of the elements in general. Several atomic weight determinations for elements other than boron, referred to in more detail later and published during the progress of this research, have evidently been undertaken with this possibility in view: but it seems desirable to state it clearly here as a primary reason for our work.

The choice of a ratio for measurement was made only after a careful review of all the known compounds of boron. Excluding borax, for the reason already given, there remain few compounds at all likely to be obtainable pure and of constant and definite composition. Among these boron trisulphide and the additive compound of boron trifluoride and ammonia seem promising, but they have been little investigated and involve methods of analysis either difficult and untried or obviously unsuited to precise work. Boron trichloride and tribromide are definite and stable compounds, the properties of which are well-known: although extremely sensitive to moisture, they appear to be the compounds best suited to precise analysis. Therefore it was decided to determine in this case the ratio $BCl_3 : 3Ag$.

Preliminary tests made by adding to a litre of pure water 1·5 g. of boric acid and 2·5 g. of silver nitrate gave a perfectly clear solution whether nitric acid (12·0 c.c. of concentrated acid) were added or not, and thus showed that silver borate is not precipitated under the conditions obtaining in the titration of a chloride with silver in presence of nitric acid by the usual procedure. Therefore the method of analysis adopted consisted in weighing boron trichloride in sealed glass bulbs, breaking the bulbs in water, and titrating the hydrochloric acid in the resulting dilute solution of boric and hydrochloric acids with silver nitrate prepared from a weighed amount of pure silver, the end-point being ascertained nephelometrically.

Weighing.

Throughout this work the special Oertling balance with the separately enclosed steel beam and the set of weights described in a previous communication (Robinson and Briscoe, this vol., p. 138) were used. The balance was kept in a darkened room having a north aspect and was illuminated by artificial light falling normally on the front of the balance. Both the zero and the sensitivity, the latter set at about 33 scale divisions per milligram, remained very constant throughout. As the inequality of the arms was very small and constant for all loads and as relative weights only were desired, all weighings and calibrations were made directly and not by reversal or substitution.

In weighing out metallic silver, etched buttons of nearly the desired weight, with pieces of pure silver wire and foil as make up, were weighed out (a valuable check) on a standard No. 7 S. W. Oertling balance, dried for 12 hours at 250° in an electrically heated glass oven, cooled beside the balance in a desiccator over solid caustic potash, transferred to the balance pan, and weighed within ½ hour. Vacuum weights of silver were ascertained by applying to the apparent weight a correction determined by the density of silver (10·49) and the density of air at the pressure and temperature observed during weighing.

The weights of boron trichloride were ascertained in the manner previously described in detail with illustrative data (Briscoe and Little, J., 1914, **105**, 1330; Briscoe, J., 1915, **107**, 72). Bulbs and stems filled with dry air were each weighed on three separate occasions against a tare, the temperature and barometric pressure being noted at the time of each weighing. After being filled and sealed off from the stem, bulbs and stems were again weighed on two separate occasions against the same tare. Then the external volume of each bulb was determined by weighing in air and in water and, the density (as the mean of concordant determinations on four samples) and actual weight of the glass of the bulb being known, the internal volume of the bulb, and hence the weight of air originally contained in the bulb was calculated. The relative vacuum weight of the boron trichloride in the bulb is evidently the apparent weight (increase in excess weight over tare) *plus* this weight of air. Before each weighing the bulbs and stems and tares were carefully wiped with well-washed pure linen and then allowed to stand in the balance case for 8—12 hours.

This method of weighing sensitive materials is evidently less well known than it should be. Weatherill (*J. Amer. Chem. Soc.*, 1924, **46**, 2442) has recently confirmed that its error is probably no greater than the error of weighing, 0·01—0·02 mg., but is apparently unaware of the prior description and use of the method by one of us, as the procedure in experiment and calculation is again described in detail and no reference is made to the prior publication.

The weights and gold half-milligram rider were repeatedly calibrated to ascertain their relative weights in air, and were always used on the same (right hand) balance pan: in all weighings, a correction was applied for the calibration error.

The error in weighing was less than 0·02 mg. and weights of boron trichloride are stated to the nearest 0·01 mg. Weights of silver are stated in the same manner, but are affected by the possible error in the nephelometric determination of the end-point, approximately 0·00005 g.

It has been stated (Manley, *Phil. Trans.*, 1913, **212**, [*A*], 227) that objects dried in an enclosed space alongside solid caustic potash can become contaminated with alkali. As this drying agent was extensively used in this and earlier determinations, the experiments described below were made to ascertain whether such contamination occurs under the conditions of the normal use of this drying agent.

As a test for alkali a solution of phenolphthalein, made very faintly pink with alkali, was used: one drop of it added to 0·05 c.c. of *N*/100-caustic soda (0·00002 g.) in 10 c.c. of water gave a distinct red coloration.

1. During more than 2 years the upper and lower compartments of the balance case had been dried by means of vessels containing caustic potash stood close against the back of the case and renewed from time to time, as the alkali deliquesced. Therefore the back pane of glass was removed from the case, flooded with about 5 c.c. of water, and the washings were tested with phenolphthalein. No trace of alkali could be detected.

2. A fairly rapid current of air saturated with water vapour was passed first through a 50% solution of caustic potash, secondly through a tower packed with solid caustic potash, and then on to the surface of about 10 c.c. of phenolphthalein solution placed in a clean wash-bottle, which had been used for distilled water for 5 years. This experiment was run continuously for 500 hours, but no trace of red coloration developed.

Therefore it is clear that caustic potash does not contaminate an air stream passed over it or glass surfaces in its neighbourhood.

Purification of Reagents.

The methods adopted for the purification of all the accessory reagents and of the main supply of silver have been sufficiently described (Robinson and Briscoe, *loc. cit.*). It is here only necessary to add that the small pieces of silver used to adjust the weights of the silver buttons were in part pieces of wire of various gauges remaining from a previous investigation (Briscoe, *loc. cit.*) and in part pieces cut from thin sheet silver with clean steel scissors, etched with nitric acid, well washed, and dried at 250°. The sheet silver was prepared by hammering and then rolling a large button of pure silver between sheets of parchment.

Three samples of silver were used, namely, Silver I, Silver A, and Silver B. The preparation of the materials A and B has been previously described (Robinson and Briscoe, *loc. cit.*). Silver I, used only in the preliminary work, was metal prepared from silver nitrate by the Stas bisulphite method and subsequently dissolved in nitric acid and reprecipitated in the same way. There is every reason to believe that the samples of silver were uniform and that A and B were closely similar : results obtained with them should, therefore, be strictly comparable. Any constant impurity in the silver would, of course, affect the absolute value of the results, but numerous investigations have shown that the method employed for preparing the silver yields a product containing but 1 part of impurity in 300,000 parts, the effect of which on the results is negligible in comparison with that of other sources of error.

Preparation and Purification of Boron Trichloride.

Sources.—The boron trichloride used in the preliminary series of analyses (sample i) was prepared from boric acid of unknown origin in stock in the laboratory. That used for the three main series was prepared from the following materials :

Sample (ii) Crude boric acid from the neighbourhood of Volterra, Tuscany.

Sample (iii) Boracite from Sultan Tchair, Asia Minor.

Sample (iv) Colemanite (calcined) from Death Valley, California, U.S.A.

We are indebted to Messrs. Borax Consolidated, Ltd., for supplies of these minerals and for detailed information as to their origin, and would here express our thanks to Mr. R. C. Baker, managing director of that company, for his personal interest in securing for us this essential starting material.

Preparation of Boric Acid.—Sample (i) was used without purification: sample (ii) was recrystallised once from a filtered solution in dilute hydrochloric acid. The boracite ($6MgO,MgCl_2,8B_2O_3$) sample (iii) and colemanite ($Ca_2B_6O_{11},xH_2O$) sample (iv) were each dissolved in boiling 1 : 1 hydrochloric acid, and the solution was diluted with its own bulk of boiling water, filtered at the boiling point in a jacketed funnel, and cooled to obtain a crop of white, crystalline boric acid, which was filtered off and dried.

Preparation of Boron Trichloride.—Dumas's method (*Ann. Chim. Phys.* 1826, [ii], **31**, 436) was tried by heating in chlorine (*a*) a mixture of ground boric oxide glass and carbon, and (*b*) charcoal soaked in hot concentrated boric acid solution, and dried; and also by striking an arc between a carbon rod and mixture (*a*) in an atmosphere of chlorine. The heating of boron nitride in chlorine and of boric oxide glass in carbon tetrachloride vapour were also investigated, but none of these methods gave a yield of boron trichloride sufficient to warrant its adoption. The heating of boric acid with phosphorus pentachloride (Gustavson, *Ber.*, 1870, **3**, 426; 1871, **4**, 975) seemed so likely to introduce volatile phosphorus chlorides as an impurity that it was not attempted. Thus it became necessary to adopt the wasteful and troublesome process of preparing and chlorinating elementary boron.

Anhydrous boric oxide was obtained by gradually feeding boric acid into a clay crucible kept at a bright red heat until the crucible was three-quarters filled, and keeping the melt at 1000°, until all evolution of steam had ceased. The resulting glass was poured on to a cold iron plate, crushed, and then ground in a Weatherhead crusher to pass a sieve of 50 meshes to the linear inch.

This oxide was then reduced with magnesium, according to the method usually attributed to Moissan, although it had been used by earlier workers (Phipson, *Proc. Roy. Soc.*, 1864, **13**, 217; Jones, J., 1879, **34**, 42; Winkler, *Ber.*, 1890, **23**, 772: see also Moissan, *Compt. rend.*, 1892, **114**, 319; Weintraub, *Trans. Amer. Electrochem. Soc.*, 1909, **16**, 165; Ray, J., 1914, **105**, 2162). A mixture of 70 parts of powdered boric anhydride with 50 parts of magnesium powder contained in a clay crucible and covered with a 2-inch layer of powdered charcoal was heated in a furnace until reaction took place. Then the air supply to the furnace was immediately cut off and the crucible and its contents were allowed to cool in a reducing atmosphere. This procedure served greatly to minimise the serious loss of boron by reoxidation, found to occur when the porous mass produced by the reaction was exposed to air whilst hot. Working details of the successful method are given, as failure attended attempts to conduct the reaction in closed vessels in an atmosphere of hydrogen and by other methods. The furnace used in all this work, a 20 lb. "Captive Fire" furnace, fired with a correct mixture of coal-gas and air, both supplied under pressure, proved specially convenient for the operations described. The coke-like product, freed from admixed lumps of charcoal, was powdered, digested for 24 hours with concentrated hydrochloric acid to decompose borides and dissolve metallic oxides present, and boiled with an equal bulk of water. After settling, the clear liquor was decanted, the residue was again twice extracted with boiling dilute hydrochloric acid and was then filtered off, washed, and dried at 100°. Some difficulty was encountered in converting this boron to the trichloride. At first, it was heated in a current of chlorine in a silica tube wound with nichrome wire and heated electrically, but it was soon found that, even at a dull red heat, the boron trichloride rapidly attacked the silica, one tube being perforated in a few hours, and the product contained considerable quantities of silicon tetrachloride. An attempt to protect the silica from attack by flooding the inner surface with concentrated magnesium nitrate solution and igniting this to oxide, thus brasquing the tube with magnesia, proved useless. An alundum tube was even more seriously attacked and was speedily blocked up by volatilised aluminium chloride: it also proved so porous as to permit a serious amount of chlorine to leak into the atmosphere: hence its use was abandoned. Ultimately, it was found that a tube of hard Jena glass, heated at about 450—500° only, by slipping over it a wider silica tube heated electrically, was scarcely attacked, could be washed out and re-used repeatedly, and gave a product almost free from silicon chloride.

Gas from a cylinder of liquid chlorine passed through a pressure gauge and safety valve consisting of a T-tube dipping into a tall jar of concentrated sulphuric acid, and then through a Drechsel bottle containing the same acid, into the reaction tube. This tube, about 36 inches long and $\frac{3}{4}$ inch in diameter, was fitted at one end with a waxed cork carrying the leading tube for chlorine: at the other end a glass adapter, attached by wide rubber tubing, led the products into a glass receiving vessel, of the form shown in Fig. 3 (R_1, R_2, etc.), cooled with solid carbon dioxide. This refrigerant was used because it was found that ordinary freezing mixtures allowed some chlorine (b. p. −33°) to pass and this carried away a considerable proportion of the boron trichloride (b. p. +12·5°). At the end of each run both tubes of the receiver were drawn down to capillaries (to permit reopening) and sealed before the blowpipe.

Another serious trouble in the earlier chlorinations was the frequent stoppage of the tubes with a white solid, which proved to be boric anhydride. Though, as others have noted (see, *e.g.*, Stock and Holle, *Ber.*, 1908, **41**, 2095), the boron was undoubtedly impure, the proportion of oxide it contained was quite insufficient to account for the quantity found in the tubes. Therefore it seemed probable that the trouble must be due to water persistently retained by the boron powder, and it was found that if this boron, immediately before chlorination, was dried by heating to redness in a silica tube in a current of dry hydrogen, the deposition of boric anhydride was so far minimised as to make the process workable: this procedure was therefore adopted throughout the preparations of boron trichloride.

Purification of Boron Trichloride.—The crude material contained considerable amounts of chlorine, hydrogen chloride, boric oxide, ferric chloride, and insoluble matters, and owing to the thoroughly unsatisfactory nature of the method of preparation many other impurities may have been present, including such volatile chlorides as chloroform, carbon tetrachloride, phosphorus trichloride, silicon tetrachloride, etc. Therefore, it was necessary to adopt a very elaborate process of purification, and as, evidently, the value of the determination wholly depends on the efficiency of this process, it must be described in detail.

The purification of sample (i) for the preliminary series was, of course, experimental and its actual treatment is sufficiently shown in Fig. 1. All the main series samples (ii), (iii), and (iv) received substantially identical treatment comprising the following stages:

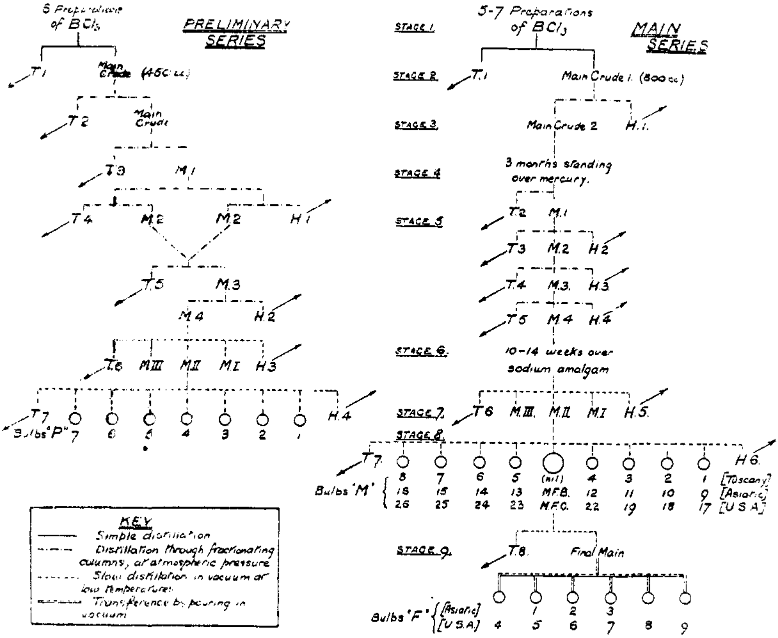
1. Distillation from various receivers into a large bulb.
2. Distillation into the single-column fractionating still.
3. Distillation in this still, with thorough fractionation, whereby chlorine and hydrogen chloride were almost completely removed.
4. Standing and frequent shaking in a sealed bulb with mercury for 3 months or longer.
5. Systematic fractional distillation in three stages, conducted in dry air at about atmospheric pressure in the "three-column still."
6. Standing and frequent shaking in a sealed bulb with sodium amalgam for about 3 months.
7. Fractional distillation into five fractions in a vacuum.

8. Fractional distillation of the middle fraction in a vacuum, and collection in bulbs.

9. In the case of samples (iii) and (iv) a middle fraction, collected among the bulbs for analysis, was further redistilled, leaving a residual fraction, and the distillate transferred to weighed bulbs by pouring.

This typical scheme of purification for the main samples is shown diagrammatically in Fig. 1. With regard to the treatment of individual samples it is only necessary to remark that the treatment of sample (ii) differed from that of (iii) and (iv) in the following details: (*a*) stage 5 comprised two separate handlings in a "two-column still" instead of one in the "three-column still" described below: (*b*) After the sample had been sealed up at the end of stage 5, it was found that the sodium amalgam had been omitted from the bulb. Fortunately, as the bulb had a "special joint," this could be rectified by transferring the contents to another similar bulb containing sodium amalgam: an attempt to effect this by distillation failed owing to the receiver becoming air-locked, but by freezing the amalgam solid in the bottom of the receiver with liquid air, it became possible to invert the apparatus and

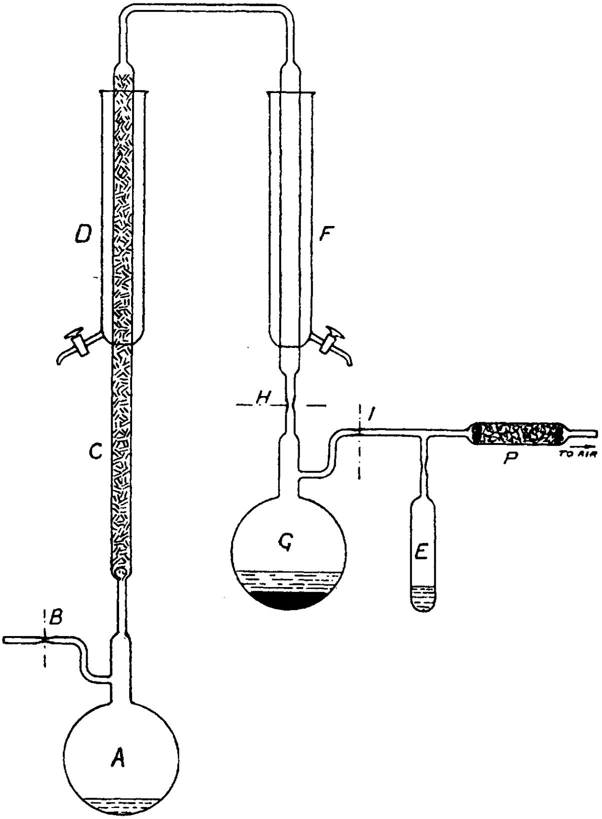
FIG. 1.



transfer the boron trichloride by pouring, and this was successfully accomplished; (*c*) the quantity of material in the final main fraction of stage 6 was little more than sufficient to fill eight bulbs and yielded a middle fraction (marked " nil," Fig. 1) too small to carry to stage 9.

The apparatus employed may be understood by reference to the " one-column " and " three-column " stills used for stages 3 and 5 of the main series purification (Fig. 1) shown in Figs. 2 and 3. The columns C were 2 cm. in diameter and 60 cm. in packed length, filled with hollow cylindrical glass beads 4 mm. in diameter and 4 mm. long (Raschig, Eng. Pat. 1914, No. 6288), supported by a perforated bulb at the bottom. The upper half of each was surrounded by a glass jacket containing water kept at 10° by stirring in crushed ice, and acted as a regulated temperature still-head.

FIG. 2.



That such columns are very efficient (see, *e.g.*, Lessing, *J. Soc. Chem. Ind.*, 1920, **40**, 115T) was confirmed by the fact that, during the first distillation, a sharp demarcation between the deep yellow chlorine and colourless boron trichloride occurred within 2 cm. in the column and moved steadily up as the last of the chlorine was removed.

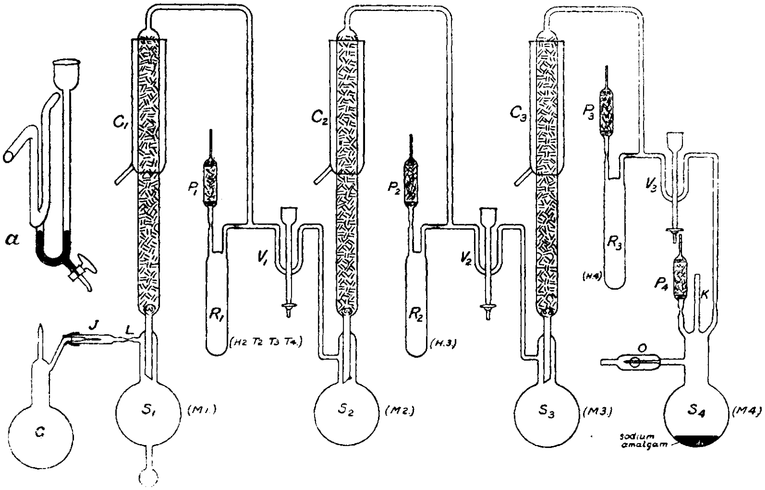
In using the " one-column still " (Fig. 2), the apparatus was filled with dry air, and then crude boron trichloride, previously collected into one vessel by distillation from the several receivers, was distilled into A *via* the side-tube, B, and this was then sealed off at the constriction. The jacket, D, having been cooled to 10°, A was immersed in water at 15—20° until the chlorine had been distilled off and swept out of the apparatus. Then, F and G being kept warm enough to prevent any condensation, a considerable head fraction was distilled into E and sealed off. Finally, F was cooled with ice and G with solid carbon dioxide, and a main fraction was distilled into G, which was then sealed off at H and I, leaving a considerable tail fraction in A. During the distillation the apparatus was open to the atmosphere through an efficient phosphorus pentoxide tube, P. In G, the boron trichloride stood, and was frequently shaken, during about 3 months in contact with pure mercury previously placed in the bulb.

The " three-column still," shown diagrammatically in Fig. 3, consisted of four bulbs, S, of 800 c.c. capacity, the first three each having a column, C, leading to a receiver, R, open to air through a phosphorus pentoxide guard tube, P, and connected *via* a mercury valve, V, to the next bulb. The whole apparatus was clamped around a single large retort-stand and sealed together. From Fig. 3a, showing the construction of the valves, it is evident how, by lowering or raising the mercury level in the U-tube, connexion between the two sides of the valve may be made or broken, and thus how it is possible to direct vapour into any desired part of the apparatus and conduct a systematic fractional distillation without bringing the boron trichloride into contact with any material other than dry glass, mercury, and air.

The valves V having been sealed with mercury, the apparatus was first dried by passing in at J a current of dry air and allowing it to pass away first through P_1, and then successively through P_2, P_3, and P_4, the capillary exit tubes being sealed or cut open as required. During this operation all parts of the apparatus in turn were repeatedly heated to 150—200°. Then a quantity of pure sodium amalgam was filtered into S_4 through the tube K, and this tube was sealed off. The current of dry air was now reversed, passing in at P_4 and out at J, and the bulb, G, containing mercury and a main fraction of crude boron trichloride from the previous distillation, was connected at J by a glass-and-rubber joint flexible enough to allow the sealed capillary of G to be broken within it. Then M 1 was cooled, the lower part in ice and the neck by a collar of solid carbon dioxide, and G was warmed at 15° until the liquid had distilled over, leaving a small tail fraction in G, which was finally sealed off at L.

The material was now completely protected against moisture, and the distillations constituting stage 5 (Fig. 1) were carried out in a manner which is obvious from Fig. 3 and the preceding description.

FIG. 3.



Rejected head and tail fractions were collected in the bulbs R, which were sealed off, immediately they had received the fractions shown (in brackets) against them, in the order R_2, R_3, R_1. The final main fraction, M 4, was collected and sealed up with the sodium amalgam in bulb S_4, provided with a "special joint," O: it stood in the bulb, and was frequently shaken, during 10—14 weeks.

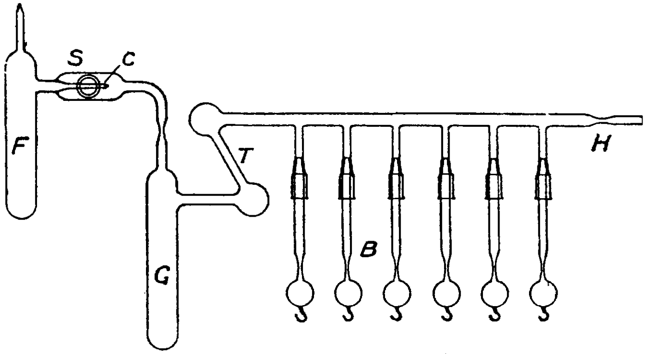
During the last distillation of this stage readings of a thermometer enclosed in the upper part of column C_3 gave readings for the boiling point of boron trichloride which, when corrected for the observed atmospheric pressure at the time of distillation, agreed closely with the value 12·5° found by Stock and Priess (*Ber.*, 1914, **47**, 3109).

The remaining stages of the purification and the transference into bulbs were carried out in a vacuum by a method essentially similar to that first described by one of us (Briscoe and Little, *loc. cit.*), and since used in several other precise investigations (see, *e.g.*, Brauner and Krepelka, *J. Amer. Chem. Soc.*, 1920, **42**, 1917; Krepelka, *ibid.*, p. 925; Baxter, Weatherill, and Holmes, *ibid.*, p. 1194; Baxter, Weatherill, and Scripture, *Proc. Amer. Acad. Arts Sci.*, 1923, **58**, 245).

The " special joint " which makes this method possible was used by one of us in the purification of vanadyl trichloride early in 1912, and was described as new in 1914, but it has recently come to our knowledge that the use of a closely similar device, though for another purpose, was described (Bruner and Bekier, *Z. Elektrochem.*, 1912, **18**, 369) prior to our publication.

One small, but important, improvement was made by interposing between the special joint, S, and the bulbs, B (Fig. 4), a two-bulb trap of the form shown at T, designed to prevent any fragments of broken glass being carried over into the bulbs by the stream of vapour when the capillary C is broken. Weatherill (*loc. cit.*) also has found this precaution desirable.

FIG. 4.



In two cases the quantity of boron trichloride in the main fraction was more than enough to fill eight bulbs, and the excess was collected as a middle fraction in a separate bulb, F (Fig. 4), and subsequently transferred to weighed bulbs in the following way.

The bulb F was fused on to the remainder of the system shown in Fig. 4 and then was heated, repeatedly evacuated, and finally sealed off at H. The special joint K was then opened, and the liquid was distilled into G, leaving a last fraction in F, which was then sealed off. The whole apparatus was next inverted and the liquid transferred to the bulbs by pouring, assisted by alternate heating and cooling of the bulbs, in alcohol at — 20° and in liquid air respectively.

This operation was performed with the material for the Final Series B and C: in both cases the tail fraction in F was carefully distilled into the side tube and left no trace of visible residue.

Tests of the Efficiency of the Method of Purification.

This is evidently a case in which the efficiency of the scheme of purification is exceptionally important and every attempt was made to secure direct experimental evidence on this point. The effect of the possible impurities upon the atomic weight is shown in Table I, whence it is evident that the elimination of boric oxide, chlorine, and hydrogen chloride is specially important.

TABLE I.

Impurity.	Change in the atomic weight of boron produced by the presence of 0·1% of the impurity in BCl_3.	B. p.
Boron trioxide, B_2O_3	+0·108	—
Chlorine, Cl_2	−0·012	−33·6°
Hydrogen chloride, HCl	−0·008	−83·1
Silicon tetrachloride, $SiCl_4$	+0·009	+59·6
Phosphorus trichloride, PCl_3	+0·017	+76
Arsenic trichloride, $AsCl_3$	+0·042	+130·2
Antimony trichloride, $SbCl_3$	+0·046	+223·5

By a fortunate chance, at a later stage of the purification of the material for the Preliminary Series, a phenomenon was observed which has, apparently, escaped the notice of other workers using boron trichloride. From mere curiosity, the residual fractions from some of the less pure samples of boron trichloride were distilled to dryness: they left a colourless, non-crystalline, and apparently gelatinous or syrupy residue which, when warmed to 40—50°, intumesced and left a white, amorphous solid. On standing in boron trichloride vapour, the solid first became translucent and then deliquesced to a liquid: it was evidently volatile with boron trichloride and probably consisted wholly or largely of boric acid or boric oxide. It was investigated by the following experiments, making use of fractions from the distillations of the Preliminary Series, transferred in a vacuum by means of special joints in the usual way.

A quantity of pure boron trichloride, leaving on evaporation practically no trace of residue, was distilled (*a*) partly on to powdered boric oxide glass, dried at 300° in a vacuum, and (*b*) partly on to boric acid dried at 100° in a vacuum. In both cases the solid dissolved and the solution yielded a distillate that left on evaporation a large, gummy residue, showing precisely the behaviour described above. Thus it was proved that boric acid and boric oxide are volatile in boron trichloride.

In order to ascertain whether this residue could be separated by distillation, a bulb, A, containing about 30 g. of boron trichloride (T 6 of the Preliminary Series) was connected by its special joint to a second evacuated bulb, B. When the liquid was distilled into B, a small but distinct residue was left in A: when the distillate in B was completely redistilled back into A, a much smaller, but still distinctly visible patch of residue remained in B. Then about one-quarter of the liquid in A was repeatedly distilled into B and *poured* back into A until no trace of residue remained on warming B. Finally, about two-thirds of the liquid was distilled into B and then redistilled back into A, when but a very small trace of residue remained in B. These observations prove that the residue can be progressively diminished by fractional distillation in a vacuum, and render it probable that it can thus be eliminated.

It is well established that mercury reacts with anhydrous chlorine : hence the prolonged treatment given in this case (until a clean surface of the metal remained bright indefinitely) should have ensured the removal of all free halogen. There exists no such evidence that anhydrous hydrogen chloride reacts with sodium amalgam, therefore a sealed bulb containing about 100 g. of clean 2% sodium amalgam and a sealed thin capillary tube containing about 0·15 g. of water were placed in a stout cylindrical bulb sealed to a closed-end mercury pressure gauge, and about 40 g. of good boron trichloride were distilled into and sealed up in the bulb. The bulb and capillary containing the amalgam and water were broken by vigorous shaking and the apparatus was set up in a room having a fairly constant temperature and kept under observation for several weeks.

There was a steady evolution of gas and rise of pressure, and this continued at a diminishing rate for more than 14 days, affording clear evidence that hydrogen chloride does react with sodium amalgam under the anhydrous conditions obtaining in the process of purification.

A separate experiment showed that pure boron trichloride had no action on sodium amalgam.

The removal of impurities was also followed analytically : about 6 c.c. of boron trichloride were decomposed with water, the solution was divided into equal parts, and these were treated (*a*) with nitric acid and (*b*) with nitric acid and ammonium molybdate, warmed, and allowed to stand several days. Several of the earlier tail fractions gave (*a*) a distinct gelatinous precipitate, probably silica, and (*b*) a slight yellow precipitate of ammonium phosphomolybdate : the later tail fractions gave no evidence whatever of silica or phosphoric acid.

Method of Analysis.

In previous determinations of the ratio of boron trichloride to silver, the bulbs have usually been broken in dilute pure ammonia. The presence of excess of ammonia, obviously desirable as a precaution against loss of hydrogen chloride if the solution has to be filtered from the fragments of the bulb, was clearly unnecessary in this case, as all the weighings requisite to determine the vacuum weight of boron trichloride had been made before the analysis was begun.

In each titration the bulb containing boron trichloride, suspended by its hook from a hooked glass rod, was washed and then lowered into about 2000 c.c. of pure water contained in a thoroughly clean resistance glass bottle of 4000—6000 c.c. capacity. The bottle was closed with its carefully fitted and polished stopper, cooled in ice for an hour to reduce the internal pressure, and then vigorously shaken to break the bulb. The reaction between boron trichloride and water was quickly over and produced a perfectly clear and colourless solution, but left some fog in the bottle: therefore the bottle was well shaken at frequent intervals until the fog had completely disappeared and then allowed to stand for at least 3 hours before it was opened.

Meanwhile a quantity of pure silver, calculated to be within a few tenths of a milligram of that required, having been accurately weighed, was dissolved in pure aqueous nitric acid (1 : 1) in a Jena glass solution flask of the special form previously described (Briscoe, J., 1915, **107**, 78), and the solution was heated to boiling, to expel nitrous fumes, cooled, and diluted to about 1200 c.c.

The stopper was carefully removed from the titration bottle and rinsed, the fragments of the glass bulb, especially the capillary ends, were broken up by means of a long, stout glass rod, and the silver solution and rinsings were transferred to the bottle *via* the side tube in the manner described in detail elsewhere.

This transference and all subsequent operations were carried out in orange light in a darkened laboratory set aside solely for these titrations and kept free from all possible sources of contamination with chlorine or silver.

The solution was gently swirled during the addition of silver and immediately thereafter the bottle was stoppered, vigorously shaken at frequent intervals during 2—3 hours, allowed to stand at room temperature for 7—10 days, being well shaken twice or thrice each day, and then packed in ice for about 48 hours.

Then 100 c.c. of the clear supernatant liquid were withdrawn with a pipette and used for duplicate nephelometric tests in the

TABLE II.

Data and Results of Analyses.

Number of analysis.	Sample of silver.	Relative vacuum wt. (g.) of BCl_3.	Relative vacuum wt. (g.) of silver.	Ratio : $BCl_3/3Ag$.	Atomic wt. of boron ($Ag = 107{\cdot}880$; $Cl = 35{\cdot}457$).	Individual and average deviations from mean.
Preliminary Series.						
P 1	Silver 1	7·10616	19·61748	0·362236	10·854	+0·002
P 2						
P 3	,, 1	8·06893	22·28012	0·362158	10·829	−0·023
P 4	,, 1	9·91393	27·37313	0·362177	10·835	−0·017
P 5						
P 6	,, 1	7·42801	20·49990	0·362344	10·889	+0·037
				Means	10·852	±0·020
Main Series.						
A. Boron from Boric Acid, Volterra, Tuscany.						
M 1						
M 2	Silver A	7·73567	21·35379	0·362262	10·862	+0·022
M 3	,, B	9·83151	27·14230	0·362221	10·849	+0·009
M 4	,, A	7·88427	21·76764	0·362201	10·843	+0·003
M 5	,, A	6·61346	18·26253	0·362133	10·821	−0·019
M 6						
M 7	,, A	7·51389	20·74865	0·362139	10·823	−0·017
M 8						
				Means	10·840	±0·014
M 9	B. Boron from Boracite, Sultan Tchair, Asia Minor.					
M 10	Silver A	7·88217	21·76472	0·362153	10·827	+0·008
M 11	,, B	7·00794	19·35154	0·362139	10·823	+0·004
M 12	,, A	11·56846	31·94600	0·362126	10·818	−0·001
M.F.B.						
M 13	,, A	12·04670	33·26752	0·362116	10·815	−0·004
M 14	,, B	11·39071	31·45640	0·362111	10·814	−0·005
M 15	,, A	8·45278	23·34215	0·362125	10·818	−0·001
M 16						
				Means	10·819	±0·004
M 17	C. Boron from Colemanite, Death Valley, California, U.S.A.					
M 18	Silver A	9·93543	27·42992	0·362212	10·846	−0·009
M 19*	,, B	6·69247	18·47861	0·362174	10·834	−0·021
M 22	,, A	6·87297	18·97723	0·362169	10·832	−0·023
M.F.C.						
M 23	,, A	8·66792	23·92939	0·362229	10·852	−0·003
M 24	,, B	8·08918	22·32812	0·362287	10·870	+0·015
M 25	,, A	5·95008	16·42010	0·362366	10·896	+0·041
M 26						
				Means	10·855	±0·019
Final Series B (from fraction M.F.B.. Main Series B).						
F 1	Silver B	5·96256	16·46538	0·362127	10·819	+0·001
F 2	,, B	5·83978	16·12666	0·362120	10·816	−0·002
F 3	,, B	5·31851	14·68670	0·362131	10·820	+0·002
				Means	10·818	±0·002
Final Series C (from fraction M.F.C., Main Series C).						
F 4	Silver B	2·94096	8·11982	0·362195	10·841	+0·001
F 5	,, A	4·86840	13·44182	0·362184	10·837	−0·003
F 6	,, A	4·89699	13·52005	0·362202	10·843	+0·003
F 7	,, A	5·72597	15·80980	0·362179	10·836	−0·004
F 8	,, A	9·24458	25·52406	0·362190	10·839	−0·001
F 9	,, B	4·69097	12·95092	0·362211	10·846	+0·006
				Means	10·840	±0·003

* Bulbs M 20 and M 21 were tares.

usual manner (Briscoe and Little, J., 1914, **105**, 1322). After an appropriate addition of silver or chloride had been made, in the form of a solution containing 0·0002 g. of silver or its equivalent per c.c., the bottle was again stoppered, shaken, and repacked in ice for 48 hours before another nephelometric test was made. When two such tests separated by 6—7 days agreed in showing that the equivalent concentrations of silver and chloride in the solutions differed by less than 2%, the titration was regarded as finished.

Statement and Discussion of Results.

Table II states the data and results for the Preliminary Series, the three Main Series, and the two Final Series. In order to examine their significance, it is important to understand the relationship of the fractions with which they were obtained; therefore the names of the fractions not analysed are included in each group, the fractions are given in order of separation, *i.e.*, in the Preliminary and the Main Series the most volatile fractions first in each group, and the results are summarised in Table III.

TABLE III.

Summary of Results.

α = *Number of Fraction* ; β = *Atomic Weight of Boron* (*deduced*).

Main Series A.

α	M 1.	M 2.	M 3.	M 4.	M.F.A. ("nil")	M 5.	M 6.	M 7.	M 8.
β	—	10·862	10·849	10·843	—	10·821	—	10·823	—

Main Series B.

α	M 9.	M 10.	M 11.	M 12.	M.F.B.	M 13.	M 14.	M 15.	M 16.
β	—	10·827	10·823	10·818	—	10·815	10·814	10·818	—

Main Series C.

α	M 17.	M 18.	M 19.	M 22.	M.F.C.	M 23.	M 24.	M 25.	M 26.
β	—	10·846	10·834	10·832	—	10·852	10·870	10·897	—

Final Series B.

α	F 1.	F 2.	F 3.
β	10·819	10·816	10·820

Final Series C.

α	F 4.	F 5.	F 6.	F 7.	F 8.	F 9.
β	10·841	10·837	10·843	10·836	10·839	10·846

The analysis of fraction M 6 was lost through an accident, but with this exception every analysis begun was completed and is recorded in the table. Both in the final transference to bulbs and in the analyses, the Series were dealt with in the order in which they are there named: the order of the analyses within each series was irregular and is immaterial.

The Preliminary Series, made with boron trichloride of unknown origin, was carried out simply to gain experience, and the variation in the results was at first supposed to have no significance, especially as the series contained but six bulbs and the *end* fractions were analysed. As the results for the Main Series A, B, and C accumulated, it was apparent that they exhibited a variation of similar type and it at once became important to ascertain whether this variation was accidental and due to errors in the analyses, or arose from a real change in the composition of the boron trichloride on distillation. By a fortunate accident, the quantity of boron trichloride in the final main fraction of the vacuum distillations of Series B and C had been much more than sufficient to fill eight bulbs, and the excess in each case had been collected as a *middle* fraction (M.F.B. and M.F.C.) in a large bulb provided with a special joint. Therefore it was determined to transfer these fractions to weighed bulbs by pouring in the manner described on p. 708, whereby, evidently, the fraction as a whole was subjected to an efficient separation from any less volatile impurity and yet any effect of distillation in causing a variation in the composition of the contents of individual bulbs was minimised. The effect of this is apparent in the average deviation from the mean in Final Series B and C, as contrasted with the corresponding figures for the Main Series A, B, and especially C. Evidently the nature and extent of the variations in the Final Series indicate that none of the analyses is likely to give an atomic weight in error by more than 0·005 and that most of the results are probably within 0·002 or 0·003 of the truth.

This being so, it follows that certain systematic variations apparent in the figures are *real* and require explanation. Three types of systematic variation may be distinguished in discussion :

(1) The last results in each series are high and in one case show a progressive increase.

(2) The first few values in each series diminish progressively to a minimum.

(3) The results in both the Main and the Final Series C are consistently higher than those in Series A and B.

Attention may first be directed to the possible impurities and their effect as illustrated by the data in Table I. The table is not exhaustive, as the possible impurities less volatile than boron trichloride clearly include higher chlorides of silicon, arsenic, phosphorus, etc., and also such compounds as chloroform and carbon tetrachloride, which, being non-hydrolysable under the conditions of analysis, would probably act, like boric oxide, as inert diluents. It is immediately evident that all impurities *less volatile* than boron trichloride tend to *increase* the apparent atomic weight, whilst chlorine and hydrogen chloride, both *more volatile* than boron trichloride, tend to *diminish* the apparent atomic weight.

The negative results of tests for silicon and phosphorus in the later tail fractions obtained in the course of purification would seem to ensure that the final main fractions could not have contained any less volatile chloride in an amount sufficient to have any perceptible effect on the atomic weight. There is not the same conclusive evidence that boric oxide was eliminated: visible traces of the gummy residue (although so small as to appear unweighable) were seen at late stages of the purification, and it seems reasonable to suppose that the increase at the ends of the series may be due to traces of boric oxide concentrated in the later fractions. This view accounts satisfactorily for the abnormally high values at the end of Main Series C, as this was much the *longest* series (the middle fraction M.F.C. being large) and the final bulbs in this case contained a considerably smaller fraction of the whole than did the corresponding bulbs in the other series.

The progressive decrease in the earlier values in the series cannot, apparently, be attributed to the presence of impurities. The concentration of volatile impurities would be greatest in the head fractions and would progressively diminish: their presence tends to lower the atomic weight, and therefore would cause a progressive *rise* in the value obtained with successive fractions. This consideration and the apparent efficacy of the chemical means used to eliminate chlorine and hydrogen chloride indicate that another explanation of this drift must be sought.

It is, we believe, to be found in the hypothesis that an isotopic separation has occurred. During the distillation into bulbs, in order to keep the pressure in the apparatus well below atmospheric pressure, the main bulk of boron trichloride was kept at or near the freezing point and the bulbs were cooled in liquid air. Under these conditions, the distillation must have been largely irreversible and, therefore, likely to effect such a separation.

Neglecting the doubtful isotope of chlorine, Cl^{39}, the elements concerned have each two isotopes and may conceivably form the eight compounds formulated below with their molecular weights and the percentage of chlorine they contain.

Compound.		Mol. wt.		% Cl.	
$B^{10}\,Cl_3^{35}$		115		91·4	
	$B^{11}\,Cl_3^{35}$		116		90·6
$B^{10}\,Cl_2^{35}\,Cl^{37}$		117		91·5	
	$B^{11}\,Cl_2^{35}\,Cl^{37}$		118		90·7
$B^{10}\,Cl^{35}\,Cl_2^{37}$		119		91·6	
	$B^{11}\,Cl^{35}\,Cl_2^{37}$		120		90·8
$B^{10}\,Cl_3^{37}$		121		91·7	
	$B^{11}\,Cl_3^{37}$		122		91·0

The lighter members of this group of compounds contain, for a given isotope of boron, a smaller percentage of chlorine than the corresponding heavier members : an increased weight percentage of chlorine causes an apparent diminution of the atomic weight : therefore a preponderance of the lighter compounds in the earlier fractions would account for the observed effect.

It should be remarked that separation in this order is determined by the difference in weight between the isotopes of chlorine. If the phenomenon under discussion is real and is due to a separation of compounds of isotopes, this order of separation affords definite evidence that in the great majority of molecules of these compounds the chlorine atoms are uniquely and permanently attached to their respective boron atoms. For if this were not so and, as is conceivable, chlorine atoms could migrate freely from one molecule of boron trichloride to another, then it is clear that for any group of B^{10} and B^{11} atoms, the chlorine in combination with either the lighter or the heavier boron atoms would, at any instant, have the same statistical average atomic weight, so that any separation by irreversible distillation would be determined solely by the relative weight of the boron atoms and would yield a series of fractions in which the atomic weight of boron would progressively increase.

This conclusion is in agreement with the work of von Hevesy and Zechmeister (*Ber.*, 1920, **53**, [*B*], 410), who have found that certain organic lead compounds in non-ionising solvents are not rendered radioactive by admixture with active lead chloride and hence conclude that no interchange of lead atoms can occur in the molecules of these compounds.

The difference in the final mean results for the three series merits more detailed consideration. The Preliminary Series and Main Series A exhibit a comparatively large variation : if the foregoing hypothesis be true, this may have been caused by a specially slow and cautious distillation of the boron trichloride in these cases, and it would follow that the values about the middle of the series should be nearest the truth. Because M 2 yielded a high value and M 6 was lost, some uncertainty attaches to any deduction from Main Series A : having regard to the effect of the middle fraction M.F.A., we are of opinion that it indicates an atomic weight about 10·825 for the Tuscany boron. Excluding the value for M 2, the mean is 10·834 with a probable error ± 0·005.

Much more definite conclusions may be drawn with regard to Series B and C. Main Series B is very consistent, the result, 10·819, probable error ± 0·0014, is scarcely changed (to 10·818, p. e. ± 0·0013) if the result M 10 is rejected.

After another distillation, the middle fraction yielded the three results of Final Series B, giving the mean value 10·818, p. e. ± 0·0008. Combining these results, we obtain the value B = 10·8183.

Main Series C is less concordant, but the explanation above suggested for the high values of M 25 and M 26 seems to justify their exclusion: the mean for the remaining four determinations is 10·841, p. e. ± 0·003: the mean including M 25 and M 26 is 10·855, p. e. ± 0·003. In this case the middle fraction, M.F.C., was much larger and gave the six concordant values of Final Series C, giving in mean 10·840, p. e. ± 0·002. Combining these results, we obtain substantially the same result, 10·8403 or 10·8407 respectively, whether the results of M 25 and M 26 are rejected or retained.

While this investigation was in progress, two other determinations of the atomic weight of boron have been published. Baxter and Scott (*Science*, 1921, **54**, 524) have stated that preliminary results obtained by the measurement of the ratios $BCl_3 : 3Ag$ and $BBr_3 : 3Ag$ indicated an atomic weight 10·83 ± 0·01. Their results have not been published in detail and cannot, therefore, be discussed in relation to our own: it is possibly significant that their result, probably obtained with boron of American origin, is comparatively high.

Hönigschmid and Birckenbach (*Ber.*, 1923, **56**, [*B*], 1467) determined the ratios $BCl_3 : 3Ag$ and $BCl_3 : 3AgCl$, using three samples of boron trichloride purified by fractional distillation in a vacuum by Stock and Kuss (*ibid.*, p. 1463). Unfortunately, the origin of their samples was, apparently, unknown. Sample I was derived from 40 c.c. of boron trichloride prepared (from boron and chlorine) and used by Stock, sometime prior to 1914, for the determination of certain physical constants (Stock and Priess, *Ber.*, 1914, **47**, 3109). Sample II was redistilled from 30 c.c. of crude material, newly made by the same method. Sample III was obtained from 50 c.c. of commercial boron trichloride. With these materials Hönigschmid and Birckenbach found the values (I) B = 10·840, (II) B = 10·818, (III) B = 10·825, which compare in striking fashion with the three results now recorded.

In calculating their final mean result, B = 10·820, they reject entirely the result B = 10·840, alleging that sample I had stood 4 months in the bulbs previous to analysis, and might have acted on the glass. In the course of our work we have repeatedly had clear evidence that no such action occurs, and our analyses, being spread, in the case of any given series, over several months, afford many clear proofs that such standing in sealed bulbs has no appreciable effect on the apparent atomic weight. Moreover, it is difficult to see how, even if some corrosion of the glass occurred, it should affect the results.

Sample I should have been the purest of the three, since it was prepared from refined material, while samples II and III were prepared from crude material by a precisely similar process. Moreover, the data obtained with Sample I are, as a series, as consistent and apparently trustworthy as those for the other samples. The rejection of the result 10·840 deduced from Series I cannot, therefore, be justified unless solely on the ground of its discordance with the other results.

Thus it appears that, though they were made with much smaller quantities of material and that, perhaps, less rigorously purified than our own, the analyses of Hönigschmid and Birckenbach confirm our finding that different samples of boron may give values for the atomic weight differing by an amount much greater than any conceivable error of the determinations. We are informed by Messrs. Borax Consolidated Ltd. that, " generally speaking, prior to 1914, boron crude materials used in Austria and Germany were boracite from Sultan Tchair (Asia Minor) or borate of lime from South America." Thus there is a certain probability that the sample (made prior to 1914) for which Hönigschmid and Birckenbach obtained the value 10·840 was derived from an American source.

The obvious conclusion from our results, thus supported, is that boron from California has an atomic weight, B = 10·840, higher by 0·02 than that of boron from Asia Minor, B = 10·820. If our interpretation of the results of Series A is correct, the boron from Tuscany (B = 10·825) is similar to that from Asia Minor.

These values indicate that the American boron contains 84% and the Eurasian boron 82% of the heavier isotope.

Comparatively few earlier investigations afford any evidence for or against the possibility of such a variation in isotope ratio as is here indicated. Substantially identical results have been found for terrestrial and meteoritic iron, nickel, and cobalt (Iron : Baxter and Thorvaldson, *J. Amer. Chem. Soc.*, 1911, **33**, 337 ; Baxter and Hoover, *ibid.*, 1912, **34**, 1657. Nickel : Baxter and Parsons, *ibid.*, 1921, **43**, 507 ; Baxter and Hilton, *ibid.*, 1923, **45**, 694. Cobalt : Baxter and Dorcas, *ibid.*, 1924, **46**, 357) and in comparing chlorine from sea water with that in several minerals (Mlle I. Curie, *Compt. rend.*, 1921, **172**, 1025) and especially with that in the ancient mineral apatite from Balme (Mlle E. Gleditsch and B. Samdahl, *ibid.*, 1922, **174**, 746).

Brönsted and Hevesy (*Nature*, 1922, **109**, 813) prepared and purified mercury from 9 minerals, from as many different sources in Europe and America, and compared the densities of these samples: they found no variation greater than the possible experimental error, corresponding to a variation of about 0·0012 in the atomic weight. More recently, Jaeger and Dijkstra (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 393) have compared the densities of samples of tetraethylsilicane prepared from twelve different sources, six meteoritic and six terrestrial, and found no evidence thus of any variation exceeding about 0·001 unit in the atomic weight of silicon.

Munro (J., 1922, **121**, 986) attempted to compare the equivalent weight of borax from the Hanmer Hot Springs, South Island, New Zealand, with that of ordinary commercial borax and could detect no difference. Unfortunately, his work is open to very serious criticism: the weights of borax were very small; the method of ascertaining this weight, by dissolving a *part* of a weighed mass of fused borax and again fusing and weighing the remainder, is objectionable; and the measurement of the *volume* of acid required for neutralisation is insufficiently precise. Further, as we have shown that fused borax is variable in composition, Munro's work must be rejected entirely.

On the other hand, Mlle Curie (*loc. cit.*) has found a value slightly above the normal for chlorine obtained from a Central African desert region, and Muzaffar (*J. Amer. Chem. Soc.*, 1923, **45**, 2009) has reported widely different atomic weights, 121·720, 122·374, 121·563, and 121·144 respectively, for samples of antimony extracted from stibnites from Peru, Bolivia, Borneo, and Hungary. Unfortunately, the method used in the latter determinations seems unsuited to precise work and does not inspire confidence in these results; and the excellent determinations of the ratio $SbCl_3:3Ag$ recently published (Sb = 121·77, Willard and McAlpine, *J. Amer. Chem. Soc.*, 1921, **43**, 797; Sb = 121·76, Hönigschmid, Zintl, and Linhard, *Z. anorg. Chem.*, 1924, **136**, 257; Sb = 121·748, Weatherill, *J. Amer. Chem. Soc.*, 1924, **46**, 2437) were made with material of unknown origin and cannot be related to Muzaffar's results.

It would seem that this evidence as a whole may be held to show that there is no inherent improbability in the variation in atomic weight now observed. It remains to be ascertained whether that variation is due to changes in the isotope ratio occurring through processes of solution, fusion, crystallisation, and volatilization occurring in the earth's crust (it may be noted that in most cases boron has probably been concentrated in the existing deposits by volatilisation, as boric acid, in steam), or whether, as Aston has suggested (*Ann. Rep.*, 1922, **19**, 272), the isotope-ratio was fixed at an earlier stage in the history of the element, possibly at the time of its formation. In the latter case, it is to be anticipated that differences in atomic weight would be most evident, as in the present case, between samples from sources so widely separated in distance that little, if any, admixture can have occurred between them.

Evidently, to answer the question here raised, more, and more precise, data are needed as to the atomic weights of elements from known sources. We therefore urge upon all who determine atomic weights that they should use only materials of definite and known origin and should seek results of the greatest possible precision, so that all such determinations may contribute in some measure to a solution of this fundamental problem of the origin of the elements.

The broad conclusions that may be drawn from this investigation may now be summarised. The present analyses agree with those of Baxter and Scott and of Hönigschmid and Birckenbach in showing that the atomic weight of boron is less than 10·85 and therefore in requiring the rejection, which we have elsewhere justified on other grounds (Briscoe, Robinson, and Stephenson, *loc. cit.*), of all the results based upon the analysis of fused borax. Two samples of boron, derived from Europe and Asia Minor, have atomic weights approximating closely to the rounded mean value *10·82*, in agreement with Hönigschmid and Birckenbach; while a sample of boron derived from North American deposits gives for the atomic weight the rounded mean value *10·84*.

The authors desire to acknowledge a grant from the Research Fund of the Chemical Society which has defrayed part of the cost of this investigation, and to express their thanks to Captain F. P. Mills, of the Northumberland and Durham Rescue Brigade, for kindly supplying the liquid air used in the distillation of boron trichloride.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE.
[*Received, January* 13*th*, 1925.]