

electrolyte at concentration  $c$  (equal to the ionic strength). Then

$$\log f = \frac{-h \sqrt{c}}{1 + ga \sqrt{c}} + Bc$$

Assume a fixed value for  $c$  and thus for  $\log f$ . To find how a slight change in the value of  $h$  will affect  $a$  and  $B$ , we differentiate, treating  $g$  as a constant, since its value has been shown to remain practically unchanged when new fundamental constants are used. Thus

$$0 = -dh \frac{\sqrt{c}}{1 + ga \sqrt{c}} + \frac{h \sqrt{c}}{1 + ga \sqrt{c}} \cdot \frac{g \sqrt{c}}{1 + ga \sqrt{c}} da + cdB$$

Hence

$$dh = \frac{hg \sqrt{c}}{1 + ga \sqrt{c}} da + \sqrt{c}(1 + ga \sqrt{c})dB \quad (1)$$

Robinson and Harned's proposed logarithmic relation between  $a$  and  $B$  is

$$\log B = 14 \log a - 9.75$$

which gives upon differentiation

$$dB/B = 14da/a \quad (2)$$

Now take a definite though hypothetical example chosen for simplicity, namely, an electrolyte for which  $ga = 1$ , or  $a = 1/g = (1/0.3289) \times 10^{-3} = 3.04 \times 10^{-3}$ . Put  $h = 0.5065$  (the value at  $25^\circ$  used by Robinson and Harned), and  $dh = 0.0038$  (the difference between 0.5065 and the newer value 0.5103). Applying equation (1) to a convenient pair of arbitrarily chosen concentrations,  $(0.1)^2$  and  $(0.3)^2$ , which are low enough for the theory to apply, we obtain

$$0.0038 = \left[ da \times \frac{0.5065 \times 0.1 \times 0.3289 \times 10^3}{1.1} \right] + [dB \times 0.1 \times 1.1]$$

and

$$0.0038 = \left[ da \times \frac{0.5065 \times 0.3 \times 0.3289 \times 10^3}{1.3} \right] + [dB \times 0.3 \times 1.3]$$

whence

$$da = 0.634 \times 10^{-8}$$

$$dB = -0.0528$$

Results such as these would, of course, have to be obtained for various pairs of concentrations and then averaged by the method of least squares. The preservation of the logarithmic relation between  $a$  and  $B$  requires, as shown by equation (2), that any increase in  $a$  should be accompanied by an increase in  $B$ , whereas we have just shown that an increase in  $a$  due to a change in the value of  $h$  is accompanied by a very great decrease in  $B$  (for alkali and hydrogen halides  $B$  is of the order 0.01 to 0.2, so  $dB$  is relatively important)."—THE EDITOR.

CHEMISTRY DEPARTMENT  
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### Crude Boron. Analysis and Composition

BY EARL H. WINSLOW AND HERMAN A. LIEBHAFSKY

When "pure" boron bought commercially began to vary widely from one lot to the next, we planned

analyses to discover why. The chemical literature was not very helpful, and we have consequently explored several ways in which such analyses can be done. The results for three commercial borons will be given below; but the experimental methods will be outlined only, and detailed literature references will be omitted. This procedure is justified because our results are not exact, because the methods may need modification to fit the particular boron being examined, and because much of the literature on elementary boron is unsatisfactory. In judging this literature, however—and in judging our work—the complexity of the boron problem should not be forgotten.

**Total Boron by Fusion.**—The sodium peroxide fusion was done in a Parr bomb with 12 g. of sodium peroxide and 1 g. of sucrose. For the carbonate-nitrate fusion, the sample was mixed in a platinum crucible with 12 g. of the fusion mixture (by weight, 2 parts sodium carbonate, 1 part potassium nitrate) and covered with 6 g. of the mixture. The crucible was heated for two hours on a hot-plate near  $700^\circ$ , then by a free flame until appreciable melting had occurred. Attack of the platinum was slight.

The fusion mixtures were dissolved and neutralized; the solutions were titrated for boron by the usual method except that a glass electrode—which is very convenient for the purpose—was used. The maximum value of  $\Delta pH/\Delta cc.$  was taken as the end-point. Any precipitate was dissolved and reprecipitated; the resulting solution was titrated for boron also. Table I shows that fine, black powders sold commercially as pure boron may contain less than 80% of that element. We have found chlorination to be an effective tool for studying the impurities present.

TABLE I

PER CENT. TOTAL BORON BY FUSION OF DRIED SAMPLES			
Sample	Boron I	"Pure" Boron	"99%" Boron
Sodium Peroxide Fusion	70	77 <sup>a</sup> 76	71 72
Carbonate-Nitrate Fusion	65	71	75

<sup>a</sup> Result from 100-mg. sample; all other samples near 25 mg.

**Rapid Chlorination.**—Very dry chlorine was passed into a vertical quartz test-tube on the bottom of which rested a quartz bucket containing the boron. A snugly fitting glass seal, through which the chlorine tube passed, prevented air or water from entering the test-tube against the issuing stream of chlorine and (later) of boron trichloride. The temperature of the sample was raised whenever glowing and fuming at a lower temperature had ceased. When no further reaction could be observed, the residues (sometimes white, sometimes gray) were weighed and examined; iron and aluminum were determined in the sublimate on the walls of the test-tube. The quartz buckets changed neither in weight nor appearance. Experiments with boric oxide showed that appreciable volatilization of this substance was not to be expected at  $725^\circ$ , the maximum temperature for these chlorinations.

TABLE II  
 RESULTS FROM THE RAPID CHLORINATION OF DRIED SAMPLES

Sample	Boron I	"Pure" Boron	"99%" Boron
No. of determinations	4	3	7
Average residue, %	14.3	60.1	23.1
Upper and lower limits, %	15.4-13.4	60.9-59.0	24.4-22.1
Sublimed chlorides	Ferric, % Fe	0.6	1.8
	Aluminum, % Al	8.6	Trace
Composition of residue	Chloride, % Cl	Trace	19.8
	Magnesium, <sup>a</sup> % Mg	...	6.8
	Boric oxide, <sup>b</sup> % B <sub>2</sub> O <sub>3</sub>	None	8.5
Spectrographic report on residue	Appreciable	B, Na, Al, Si	B, Mg, Si
	Traces	Ca, Mg	Mn, Cu, Ca

<sup>a</sup> Calculated from results of chloride determination. Qualitative tests showed magnesium present in approximately the expected amounts. <sup>b</sup> Boric oxide reported here is that extracted by hot water.

**Slow chlorination.**—Additional information was sought by chlorinating more slowly 100-mg. samples of boron in a horizontal reaction train. The less volatile reaction products, such as ferric and aluminum chlorides, condensed in the train before they reached two gas washing bottles, which contained water initially. Boron trichloride was absorbed and hydrolyzed in these washing bottles, the solutions in which were eventually titrated for hydrochloric and boric acids; the glass electrode was used here also.

Despite space limitations, it seems well to point out that chlorine can complicate these acid determinations in several ways. These complications were finally minimized by wrapping the washing bottles with black cloth (to prevent photochemical reactions during the chlorination); by shaking the solution from a washing bottle with excess mercury (to extract the residual chlorine), mercury and mercurous chloride being removed and washed before the solution and washings were titrated; and by carrying out the chlorine extraction immediately a run was finished. Runs made without boron showed blank corrections to be small.

The results of this work are given in Table III. The residues were usually light gray.

TABLE III

SLOW CHLORINATION DATA FOR DRIED 100-MG. SAMPLES

	Boron I		"Pure" Boron		"99%" Boron	
BCl <sub>3</sub> liberated, as						
% B	59.0	56.7 55.8	60.5 65.5	59.7 62.3		
% Residue <sup>a</sup>	..	20.8 22.5	59.2 56.8	23.1 21.9		
Moles HCl/moles						
H <sub>2</sub> BO <sub>3</sub>	3.16	3.05 3.17 <sup>b</sup>	2.95 3.01 <sup>b</sup>	2.83 3.00 <sup>b</sup>		

<sup>a</sup> Residues should have compositions corresponding to those of Table II. <sup>b</sup> Obtained by final, improved method.

Boron trichloride seems to be the only boron compound and the only acid-producing substance reaching the washing bottles in appreciable amount. (In all our chlorination work, the sublimed reaction products could have included small amounts of volatile boron compounds.) We believe that Table III truly gives the percentage of the sample converted to boron trichloride; this percentage is in every case appreciably smaller than the per cent. total boron in Table I; it probably includes all the boron present as the element and as metallic borides.

According to Table II, the percentage of the samples volatilized out of the test-tube during rapid chlorination is  $100 - (14.3 + 0.6 + 8.6) = 76.5$  for Boron I;  $(100 +$

$19.8) - (60.1 + 1.8) = 57.9$  for "Pure" Boron; and 91.6 for "99%" Boron. For "Pure" Boron, this percentage agrees with the % B in Table III; but in the other cases it is appreciably greater.

Spectrographic examination of our samples showed carbon to be absent. The analytical results (Tables I and II) show that some element (presumably oxygen) not listed in Table II must be present in appreciable amount. The data of the preceding paragraph point to a possible volatilization of lower boron oxides or oxychlorides during the chlorination of Boron I and of "99%" Boron; that this could have escaped observation has been mentioned.

As a matter of historical interest, we examined the small quantity available of a pinkish beige powder<sup>1</sup> labeled "Weintraub B<sub>2</sub>O 1908." Fusion gave 76.3% total boron. Rapid chlorination gave 3.4% residue, 0.06% iron. Spectrographic report on the residue: B, high; Si, present; Mg, trace. We do not consider that the existence of B<sub>2</sub>O has been established.

We wish to emphasize finally that materials sold commercially as pure boron may contain less than 80% total boron, much of which is not present as the element. The most likely impurities are oxygen and whatever reducing agent (in our cases, magnesium, aluminum) was used in the preparation. We hope that the methods outlined here will prove useful in further work on the problems of crude boron.

(1) Cf. Weintraub, *Trans. Electrochem. Soc.*, **16**, 165 (1909).

RESEARCH LABORATORY  
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## NEW COMPOUNDS

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### *sym-p,p'*-Dichlorotetraphenylethylene

Treatment of 100 g. of *p*-chlorobenzophenone with 100 g. of phosphorus pentachloride at 150° according to Overton<sup>1</sup> yielded 110 g. (90%) of *p*-chlorobenzophenone chloride;

(1) Overton, *Ber.*, **26**, 28 (1893).