The increasing practical and theoretical importance of the chemistry of boron has attracted the attention of numerous research workers. Direct measurements of the heat of formation of boron oxide have been made, but the values reported by different workers differ considerably from each other. Roth and Borger [1], who combusted boron in oxygen, found that the heat of formation of the vitreous oxide was 340 ± 3 kcal, corrected by Roth in 1914 [2] to 339 ± 2.3 kcal. This value is in close agreement with that reported by Todd and Miller [3], viz., 335 ± 0.8 kcal, for spectroscopically pure boron. In 1940, however, Eggensgheers, Monroe, and Parker [4] repeated the work on direct measurement of the heat of formation of vitreous B2O3, which they found to be 321.1 ± 3.1 kcal. They observed the difference between their result and those of Roth and Borger and of Todd and Miller to contamination of the samples of boron with hydrides of boron.

Johnston, Hersch, and Kent [5], in a paper devoted chiefly to the determination of the specific heat of elementary boron at low temperatures, derive the heat of formation of crystalline B2O3 (502.0 ± 3.4 kcal) from the summation of the thermal effects of five processes, including the heat of hydrolysis of diborane, which is, according to Roth and Borger [1] equal to 168.1 kcal.

Southard [6] determined the heat of dissolution of vitreous and crystalline B2O3 in water at 25°C (1000 mole of water per mole of B2O3), finding values of 7.82 and 3.48 kcal per mole respectively. The heat of transformation of vitreous into crystalline B2O3 is thus 4.33 kcal per mole, according to Southard. According to Artsdalen and Anderson [7] the heat of dissolution of vitreous B2O3 in water at 25°C (1110 mole of water per mole of B2O3) amounts to 7.22 ± 0.25 kcal per mole, and it is only very slightly dependent on the final concentration of the solution. The value for infinite dilution is 7.250 kcal per mole.

Only one value for the heat of formation of gaseous BCl3 is known to us, viz., that of Trosch and Heute-seullle [8], who in 1870 reported a value of 104 kcal. The heat of hydrolysis of gaseous BCl3 (910 mole of water per mole of BCl3) amounts, according to these authors, to 79.2 kcal per mole. Berthelot later found [9] that the heat of hydrolysis of liquid BCl3 (650 mole of water per mole of BCl3) at 1°C is 65.8 kcal per mole, and that its latent heat of vaporization is 4.5 kcal per mole. According to Berthelot the heat of hydrolysis of gaseous BCl3 is 70.3 kcal per mole. Roth [2] found as the heat of formation of BCl3 as being 104 kcal.

We have determined the heat of hydrolysis of gaseous BCl3 by a method depending on passing the gas through water at 25°C in a calorimeter with an insulating envelope. Knowing the heat of hydrolysis of BCl3 we can calculate from the heat of formation of B2O3 the heat of formation of BCl3. As will be shown below, it is possible from this to arrive at the correct value for the heat of formation of boron oxide.

EXPERIMENTAL

The boron chloride in our possession was contaminated with chlorine, as was evident from its green color. It was purified with the aid of metallic mercury at 0°C. The purity of the product so obtained was shown by the results of analysis of the solutions obtained in the calorimetric experiments; the mean molar ratio of HCl to H2SO4 in the solutions was 3.105, which corresponds with a purity of 99.67% for the BCl3.

The heat of hydrolysis was measured in a calorimeter with an insulating envelope [10]. The envelope was kept at a temperature of 25°C ± 0.01°C. Hydrolysis was conducted in a glass calorimeter beaker of about 400 ml capacity. The experiments were performed as follows: the glass tube 5 (volume about 80 ml) is filled with BCl3 vapor, and the tube is fitted into the circuit shown in Fig. 1. In the initial stage, air enters from a gasometer at 1, and is dried in the wash-bottles 2 and 3, containing sulfurous acid and phosphorus pentoxide, respectively, before going through the by-pass tube (tap 4 open, taps 5 and 7 shut) and the spiral 8, where it assumes the
temperature of the thermostatic envelope of the calorimeter, and then through the injector 9 into the calorimeter vessel containing water.

After completion of the initial stage of the experiment, tap 4 is closed, and taps 6 and 7 are opened, when the boron chloride in 5 is swept out into the calorimeter by a stream of dry air, entering the solution in the form of small bubbles, full absorption of which is facilitated by the action of the stirrer 10. The same amount (557 g) of bi-distilled water is taken in all cases. The final concentration of the solution amounted to about 6600 mol of water per mol of BC13.

The rise in temperature was measured by means of a Beckmann thermometer, calibrated by the All-Union Institute of Standards to an accuracy of 0.0007° readings were taken every 30 sec. The maximum period of the reaction lasted about 2-3 min. The rise in temperature amounted to 0.5-0.6°, and the rate of rise of temperature in the initial and final periods was 0.005-0.006° per min. Calorimeter corrections (for radiation, heat of vaporization of water, heat evolved by the stirrer) were calculated by the Regnault-Planck-LeRoy formula, and amounted to 2-5% of the observed temperature rise. The method of determining the water equivalent of the calorimeter was the same as that previously described [10].

The solutions obtained were analyzed volumetrically, HCl by titration with NaOH with methyl orange indicator, followed by titration of H3BO3 with phenolphthalein indicator after addition of mannitol [11]. Since the titrations of HCl were the more accurate, the number of moles of hydrolyzed BC13 was taken as being equal to one third of the number of moles of HCl formed. The accuracy of the final results for the heat of hydrolysis of BC13 is about 1.5%. The results obtained are given in Table 1.

**Table 1**

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Temp. rise (°C)</th>
<th>No. of Millimoles</th>
<th>HCl</th>
<th>H3BO3</th>
<th>Heat of hydrolysis in kcal per mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.551</td>
<td>8.637</td>
<td>2.73</td>
<td>2.689</td>
<td>2.94</td>
</tr>
<tr>
<td>2</td>
<td>0.554</td>
<td>8.636</td>
<td>2.96</td>
<td>2.965</td>
<td>3.00</td>
</tr>
<tr>
<td>3</td>
<td>0.534</td>
<td>8.566</td>
<td>3.21</td>
<td>3.223</td>
<td>3.01</td>
</tr>
<tr>
<td>4</td>
<td>0.521</td>
<td>8.566</td>
<td>2.78</td>
<td>2.845</td>
<td>3.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mean: 80.8</td>
</tr>
</tbody>
</table>

where \( Q_{H_3BO_3} \) is the heat of formation of \( H_3BO_3(\text{gaseous}) \).

According to Ansdalen and Andersen [7]

\[
B_2O_3(\text{v. e.}) + 3H_2SO_3(\text{g.}) = 2H_3BO_3(\text{g.}) + 7.96 \text{ kcal}
\]

and hence

\[
Q_{H_3BO_3} = \frac{1}{2} Q_{SO_3} + 105.5 \text{ kcal.}
\]

The heat of formation of BC13 can be derived from the heat of hydrolysis of gaseous BC13, so found:

\[
BCl_3(\text{g.}) + 6H_2O(\text{liquid}) = H_3BO_3(\text{g.}) + 2HCl(\text{g.}) + 80.8 \text{ kcal.}
\]

Knowing the heats of formation of liquid water and HCl [12], which are 68.37 and 38.61 kcal, respectively, we obtain for the heat of formation of gaseous BC13

\[
Q_{BCl_3} = Q_{H_3BO_3} - 167.1 \text{ kcal.}
\]

\[\text{(1)}\]

* The figures in parentheses signify concentrations, expressed as moles of water per mol of dissolved substance.