

Heat of Formation of Boron Trichloride

Walter H. Johnson, Richard G. Miller,¹ and Edward J. Prosen

The heat of formation of gaseous boron trichloride has been determined by the direct reaction of gaseous chlorine with amorphous boron in a calorimeter.



$$\Delta H_f^\circ(25^\circ \text{C}) = -407.98 \pm 1.34 \text{ kJ/mole } (-97.51 \pm 0.32 \text{ kcal/mole}).$$

By utilizing the values previously reported for the heats of formation of boric acid, diborane, and pentaborane, the heat of hydrolysis of boron trichloride and the heats of reaction of diborane and pentaborane with chlorine have been obtained. By the use of an estimated value for the heat of sublimation of boron, the average bond energy of the B-Cl bond in boron trichloride is found to be 105.2 kcal at 0° K. The data on the heats of formation of diborane, boric oxide, boric acid, and boron trichloride now form a consistent set of values.

1. Introduction

The heat of formation of boron trichloride has long been uncertain because of the fact that calculation of it has been dependent upon uncertain values of the heat of formation of boric oxide or boric acid. Since new values have been determined for the heat of formation of boric oxide through the heat of decomposition of diborane [1]² and the heat of reaction of diborane with water [2], it seemed desirable to make a direct determination of the heat of formation of boron trichloride. This latter value, when combined with the heat of hydrolysis of boron trichloride and with auxiliary data, yields an independent value for the heat of formation of boric oxide. The consistency in the values thus obtained is very strong evidence for the accuracy of the heats of formation of boric oxide, boric acid, diborane, and boron trichloride.

An accurate value for the heat of formation of BCl_3 provides useful information regarding the energy of the B-Cl bond and permits the calculation of the heat of reaction of boron hydrides with chlorine.

2. Method

The substitution method of calorimetry was used. The quantity of electrical energy required to produce a certain rise in the temperature of the calorimeter system was determined in one series of experiments. In a second series the temperature rise was duplicated, but a substantial part of the energy was derived from a precisely measured quantity of the chemical reaction. The calorimeter system was identical in both series except for the reacting chemicals. By this method the energy liberated by the chemical reaction is obtained directly in terms of electrical energy.

3. Materials and Apparatus

The boron was prepared by the thermal decomposition of diborane by passing diborane diluted with helium through a quartz tube heated to 600° C [1]. The amorphous boron was removed from the tube, placed in a tantalum combustion boat, and heated for 1 hr at about 700° C at a pressure of less than 1×10^{-5} mm of mercury. Spectrochemical examination of the boron by the Spectrochemistry Section of the Bureau showed only negligible traces of metal impurities. The effect of a small amount of hydrogen remaining in the boron was calculated to be less than the estimated uncertainty of the measurements.

The chlorine, obtained from the Matheson Company, was about 99 percent pure; the chief impurity was 0.9 percent of carbon dioxide. It was dried by passing over phosphorus pentoxide. The helium was purified by heating it to 600° C in a copper-oxide furnace and directing it successively through Ascarite, anhydrous magnesium perchlorate, and phosphorus pentoxide.

A section of the calorimetric vessel is shown in figure 1. It consisted of a quartz tube *A* closed at the bottom and fitted with a manganin heating coil *B* surrounded by a silver shield *C* and a vacuum jacket *D*. The boron sample was placed in the quartz crucible *E*, and the chlorine introduced through the quartz tube *F*. The exit gases passed through the glass helix *G*, in which they were cooled to calorimeter temperature.

The calorimeter was of the isothermal jacket type described in a previous paper [2]. Calorimeter temperatures were measured by means of a platinum resistance thermometer in conjunction with a G-2 Mueller bridge and a galvanometer of high sensitivity. Readings on the galvanometer scale were made to the nearest 0.5 mm which was equivalent to 50 $\mu\text{deg C}$. The electrical energy was obtained from a 120-v storage battery from which no other current was drawn during these experiments. The quantity

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² Figures in brackets indicate the literature references at the end of this paper.

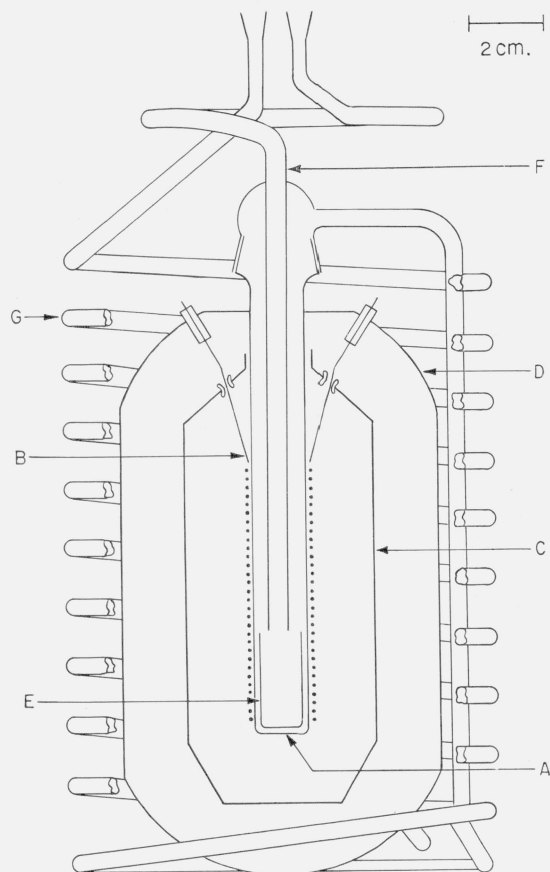


FIGURE 1. Calorimetric reaction vessel.

of electrical energy was determined from the electrical current through the heating coil, the potential drop across the coil and the time of passage of the current. The current and potential measurements were obtained from the potential drop across appropriate standard resistors included in the power circuit. The potentials were measured with a Wenner potentiometer which was balanced against a thermostated Weston standard cell [3]. Timing of the experiments was accomplished by reference to the standard second signals produced at the Bureau. All equipment was calibrated in the Bureau laboratories.

4. Procedure

A sample, 0.25 to 0.50 g, of the finely divided amorphous boron was pressed into a pellet, placed in the weighed quartz crucible, and the apparatus assembled. A constant stream of helium was passed through the system during the entire experiment. After the initial rating period, during which temperatures were observed at regular intervals, the vessel was heated electrically to about 400° C and the chlorine introduced. The reaction started and proceeded smoothly. When the desired calorimeter temperature was reached the electric current was interrupted, the chlorine bypassed, and the system

allowed to come to equilibrium. Temperatures were then observed at regular intervals during a final rating period.

The rates of flow of the helium and chlorine were determined with capillary flowmeters. The temperatures of the chlorine and helium were taken as the mean room temperatures during the time of flow. The flow rates and temperatures of the chlorine and helium were required only for making the small heat capacity correction. The amount of chemical reaction was determined from the difference between the mass of boron sample and that of the residue remaining in the crucible at the end of the experiment.

The system was calibrated in the same manner except for the omission of the boron and chlorine. In each case the quantity of electrical energy was carefully measured and the initial and final temperatures of the calorimeter were reproduced as closely as possible.

5. Results

The results of the electrical calibration experiments are given in table 1. E is the electrical energy added to the system. ΔR_c is the temperature rise corrected for heat leakage and heat of stirring and expressed in ohms increase in resistance of the platinum resistance thermometer as measured on the resistance bridge. E_s is the energy equivalent of the calorimeter expressed in joules/ohm.

TABLE 1. Results of the electrical calibration experiments

Experiment number	ΔR_c	E	E_s
	<i>ohm</i>	<i>j</i>	<i>j/ohm</i>
1	0.286106	59088.3	206526
2	.286667	59161.3	206376
3	.284978	58829.9	^a 206373
4	.287584	59334.5	206321
Mean			206399
Standard deviation of the mean			± 44

^a This value includes a correction of -64.0 j/ohm because of a change in the calorimetric system.

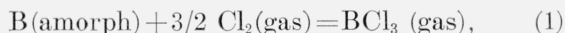
The results of the calorimetric reaction experiments are given in table 2 where ΔR_c is the corrected temperature rise of the calorimeter system, q , the product of E_s and ΔR_c , is the total heat absorbed by the system, E is the electrical energy added, q_g is the correction for the heat capacities of the re-

TABLE 2. Results of the calorimetric reaction experiments

Experiment number	ΔR_c	q	E	q_g	Boron reacted	$-\Delta H_f$ (25° C)
	<i>Ohm</i>	<i>j</i>	<i>j</i>	<i>j</i>	<i>g</i>	<i>kJ/mole</i>
1	0.287323	59303.2	49172.7	-0.4	0.26876	407.86
2	.302977	62534.1	46119.0	-2.8	.43684	406.65
3	.291356	60135.6	47954.0	-3.5	.32216	409.24
4	.305550	63065.2	44643.5	-5.8	.48890	407.83
Mean						407.90
Standard deviation of the mean						± 0.53

actants and products in converting to the isothermal process at 25° C, and $-\Delta H_f$ is the heat evolved by the chemical reaction at 25° C.

The mean value for the heat of reaction as given in table 2 was converted to kcal/mole, using 10.82 for the atomic weight of boron and 4.1840 j as the equivalent of 1 cal. A correction of 0.02 kcal/mole was applied to convert the gases to their thermodynamic standard states. The following heat of reaction was obtained:

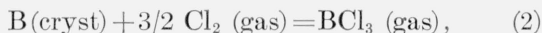


$$\begin{aligned} \Delta H_{298.15}^\circ &= -407.98 \pm 1.34 \text{ kJ/mole,} \\ &= -97.51 \pm 0.32 \text{ kcal/mole.} \end{aligned}$$

The uncertainty has been taken as twice the standard deviation of the mean of the experimental values combined with reasonable estimates of all known sources of error.

6. Derived Data

By the use of the heat of transition of crystalline to amorphous boron as 0.4 kcal/mole (estimated [4]), we obtain for the heat of formation of boron trichloride from crystalline boron:

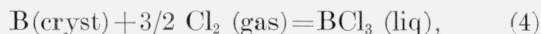


$$\begin{aligned} \Delta H_{298.15}^\circ &= -406.31 \pm 1.34 \text{ kJ/mole,} \\ &= -97.11 \pm 0.32 \text{ kcal/mole.} \end{aligned}$$

By the combination of (1) and (2) with the heat of vaporization of boron trichloride (5.6 ± 0.1 kcal/mole [4]) there is obtained for the liquid:

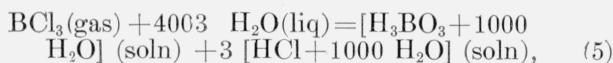


$$\begin{aligned} \Delta H_{298.15}^\circ &= -431.41 \pm 1.42 \text{ kJ/mole,} \\ &= -103.11 \pm 0.34 \text{ kcal/mole, and} \end{aligned}$$

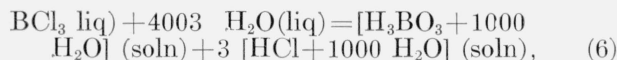


$$\begin{aligned} \Delta H_{298.15}^\circ &= -429.74 \pm 1.42 \text{ kJ/mole,} \\ &= -102.71 \pm 0.34 \text{ kcal/mole.} \end{aligned}$$

By combination of the value obtained for eq (1) with the values recently reported from our laboratory for the heat of decomposition of diborane ($\Delta H = -6.73 \pm 0.52$ kcal/mole [1]), its heat of reaction with water ($\Delta H = -111.46 \pm 0.54$ kcal/mole [2]), and with the heat of formation of aqueous hydrochloric acid ($\text{HCl} \cdot 1000\text{H}_2\text{O}$; $\Delta H_f^\circ = -39.808 \pm 0.010$ kcal/mole [6]), we obtain for the heats of hydrolysis of boron trichloride:



$$\begin{aligned} \Delta H_{298.15}^\circ &= -310.79 \pm 1.84 \text{ kJ/mole,} \\ &= -74.28 \pm 0.44 \text{ kcal/mole, and} \end{aligned}$$

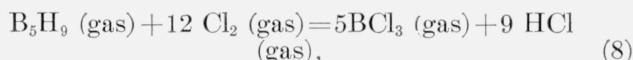


$$\begin{aligned} \Delta H_{298.15}^\circ &= -287.36 \pm 1.84 \text{ kJ/mole,} \\ &= -68.68 \pm 0.44 \text{ kcal/mole.} \end{aligned}$$

By combining the value recently obtained for the heats of decomposition of diborane and pentaborane [1] with the value from the present investigation and the heat of formation of gaseous hydrogen chloride [6], we obtain for the heats of reaction of diborane and pentaborane with chlorine:



$$\begin{aligned} \Delta H_{298.15}^\circ &= -1398.00 \pm 2.89 \text{ kJ/mole,} \\ &= -334.13 \pm 0.69 \text{ kcal/mole, and} \end{aligned}$$



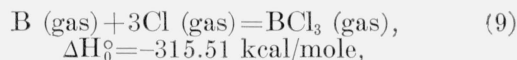
$$\begin{aligned} \Delta H_{298.15}^\circ &= -2925.08 \pm 3.43 \text{ kJ/mole,} \\ &= -699.11 \pm 0.82 \text{ kcal/mole.} \end{aligned}$$

We have combined the value given for eq (2) with the following values for $H_{298.15}^\circ - H_0^\circ$ in kcal/mole:

$\text{BCl}_3(\text{gas})$	3.362	[7]
$\text{B}(\text{cryst})$	0.290	[7]
$\text{Cl}_2(\text{gas})$	2.194	[8]

and have obtained -96.89 kcal/mole for the heat of formation of $\text{BCl}_3(\text{gas})$ at 0° K.

The heat of sublimation of boron has been calculated from vapor pressure data [9] to be 133 ± 4 kcal/mole at 0° K. If the heat of dissociation of $\text{Cl}_2(\text{gas})$ is taken as 57.08 kcal/mole [8], these data give for the reaction:



from which the average bond energy is calculated to be 105.2 kcal.

7. Prior Investigations

In the following treatment of the previously reported data, several corrections have been applied to reduce the data to a comparable basis. The data for the hydrolysis reaction (eq 6) have been converted to 25° C with an estimated temperature coefficient of -150 cal/deg mole. The heats of formation of HCl and H_3BO_3 in the resulting solution have been taken as those of the aqueous acids of the same concentration [6]; this assumes that the heat of mixing of these acids is negligible at high dilutions [10, 11, 12]. For ease in comparison, the tabulated heats of hydrolysis have been corrected to final concentrations of $\text{H}_3\text{BO}_3 \cdot 1000\text{H}_2\text{O}$ and $\text{HCl} \cdot 1000\text{H}_2\text{O}$. All values are based on the 1956 International Atomic Weights [13].

Troost and Hautefeuille [14] passed chlorine over amorphous boron and hydrolyzed the resulting BCl_3 . In a separate experiment they hydrolyzed liquid BCl_3 to a solution of the same final composition ($\text{H}_3\text{BO}_3 \cdot 3\text{HCl} \cdot 900\text{H}_2\text{O}$). For the first reaction they report as the mean of six experiments: $\Delta\text{H} = -183.2$ kcal/mole BCl_3 ; for the second, $\Delta\text{H} = -79.2$ kcal/mole. No details are given by Troost and Hautefeuille as to the temperature at which they carried out their experiments, however they used the same mercury calorimeter as Favre and Silberman [15] and apparently used the same conditions. Favre and Silberman also do not specify their working temperatures but there are some indications in their papers that it was about 20°C . We have assumed this to be the case; thus, the values obtained by Troost and Hautefeuille corrected to the specified conditions give $\Delta\text{H} = -183.7$ kcal/mole for the formation reaction and $\Delta\text{H} = -80.0$ kcal/mole for the hydrolysis reaction. The standard heats of formation of BCl_3 (based on crystalline boron as the standard state) calculated from these data are -103.3 kcal/mole for the direct combination and -91.4 kcal/mole for the hydrolysis method.

Considerable doubt has been cast upon these data from the observations by Berthelot [16] and Thomsen [17] that Favre and Silberman obtained values for the heats of neutralization of hydrochloric, hydrobromic, hydriodic, and nitric acids by both potassium and sodium hydroxides that were much higher than the accepted values, although exhibiting reasonable concordance among themselves. This suggests that there was some systematic error, probably in their calibration. An examination of their data [15] for these, as well as for other reactions indicates that the reported values should be reduced by about 11 percent. If Troost and Hautefeuille used the same calorimetric system with the same calibration, which they imply, then the same correction should be applied to their data. This would reduce the value for the heat of formation of BCl_3 (liq) obtained from the combination of the two reactions to -91.9 kcal/mole. The heat of hydrolysis then becomes -71.2 kcal/mole, which leads to -100.2 kcal/mole for the heat of formation of liquid BCl_3 . This correction is admittedly only approximate and the values so obtained are quite uncertain.

There is no information regarding the purity of the amorphous boron used by Troost and Hautefeuille; however, the boron available at that time was undoubtedly quite impure. On the other hand, reasonably pure BCl_3 could be prepared; for this reason their data for the hydrolysis reaction should be more reliable than that which they obtained from the direct combination.

Berthelot [16] obtained -65.8 kcal/mole for the heat of hydrolysis of liquid BCl_3 at 10°C . When corrected for temperature and concentration the heat of hydrolysis becomes -68.6 kcal/mole, which gives -103.2 kcal/mole for the heat of formation of liquid BCl_3 .

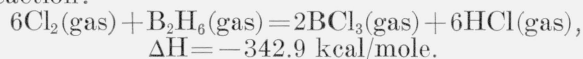
Laubengayer and Sears [18] studied the same reaction at 0°C in an ice calorimeter and reported two values for different final concentrations. Both values, when corrected for temperature and concen-

tration, give -69.3 kcal/mole for the heat of hydrolysis and -102.1 kcal/mole for the heat of formation of liquid BCl_3 .

Kapustinskiĭ and Samoilov [19] have measured the heat of solution and hydrolysis of gaseous BCl_3 at 25°C . Their data give -90.7 kcal/mole for the heat of formation of BCl_3 (gas).

Skinner and Smith [20] determined the heat of hydrolysis of liquid BCl_3 at 25°C to be -69.2 kcal/mole, which gives -102.2 kcal/mole for the heat of formation.

Lacher, Scruby, and Park [21] measured the heat of reaction for the gas-phase chlorination of diborane, to yield BCl_3 and HCl at about 80°C . We have corrected this value to 25°C and obtained for the reaction:



This leads to -101.5 kcal/mole for the heat of formation of BCl_3 (gas).

The values for the heats of hydrolysis and the corresponding standard heats of formation of liquid BCl_3 are summarized in table 3. The crystalline form of boron at 25°C has been taken as the standard reference state. Values reported for the heat of formation of BCl_3 (gas) have been converted to correspond to the liquid using 5.6 kcal/mole [5] for the heat of vaporization. It is apparent that the agreement among the results of Berthelot, Laubengayer and Sears, Skinner and Smith, and the present investigation is good.

TABLE 3. Heats of hydrolysis and formation of BCl_3 (liquid)

Investigators	ΔH hydrolysis	ΔH°
Troost and Hautefeuille [14]:		
Direct reaction	<i>kcal/mole</i>	<i>kcal/mole</i>
Hydrolysis	-80.0	-103.3
Direct reaction, corrected		-91.4
Hydrolysis, corrected		-91.9
Berthelot [16]	-71.2	-100.2
Laubengayer and Sears [18]	-68.2	-103.2
Kapustinskiĭ and Samoilov [19]	-69.3	-102.1
Skinner and Smith [20]	-75.1	-96.3
Lacher, Scruby, and Park [21]	-69.2	-102.2
Present investigation		-107.1
		-102.7

8. Discussion

Most of the thermochemistry of the boron compounds involves the heat of formation of boric oxide (or of boric acid); a reliable value for this constant is therefore quite important. As we have stated previously [2], values reported for the heat of formation of boric oxide range from -280 to -370 kcal/mole. Most of these values were obtained by the combustion of amorphous boron in an oxygen bomb calorimeter; the difficulties and unreliability of such experiments have been analyzed [2]. Nathan [22] obtained -306 ± 3 kcal/mole for the complete combustion of boron in an oxygen bomb calorimeter. We have obtained -305.3 ± 0.8 kcal/mole for the standard heat of formation of boric oxide from the

heat of decomposition of diborane and the heat of reaction of diborane with water [2]. The latter value is in reasonably good agreement with that reported by Roth, Börger, and Bertram [23].

An independent value for the heat of formation of boric oxide may be obtained from the heat of chlorination of boron and the heat of hydrolysis of the resulting BCl_3 . The only previous data leading to a value for the heat of formation of BCl_3 that do not involve boric oxide are those of Troost and Hautefeuille, discussed above. The uncertainties regarding their materials, apparatus, and calibration make this value very unreliable.

We have determined directly the heat of formation of BCl_3 to obtain an independent value for the heat of formation of B_2O_3 , and to resolve the discrepancy in the values reported for the heat of formation of BCl_3 . If the value for the heat of formation of BCl_3 obtained in this investigation is combined with the heat of hydrolysis reported by Skinner and Smith [20], there is obtained -306.3 kcal/mole for the standard heat of formation of boric oxide. This is in good agreement with the value obtained from the diborane data.

In view of the general agreement among the values obtained by different methods it can be stated that the data available for the heats of formation of diborane, boric oxide, boric acid, and boron trichloride form a consistent set of values.

9. References

- [1] E. J. Prosen, W. H. Johnson, and F. Y. Pergiel, *J. Research NBS* **61**, 247 (1958) RP2901.
- [2] E. J. Prosen, W. H. Johnson, and F. Y. Pergiel, *J. Research NBS* **62**, 43 (1959) RP2927.
- [3] E. J. Prosen, F. W. Maron, and F. D. Rossini, *J. Research NBS* **46**, 106 (1951) RP2181.
- [4] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, Selected values of chemical thermodynamic properties, NBS Circ. **500** (U.S. Government Printing Office, Washington 25, D.C., 1952).
- [5] W. H. Evans, D. D. Wagman, and E. J. Prosen, NBS (private communication).
- [6] W. H. Evans and D. D. Wagman, NBS (private communication).
- [7] W. H. Evans, E. J. Prosen, D. D. Wagman, *Thermochemistry and thermodynamic functions of some boron compounds, thermodynamic and transport properties of gases, liquids, and solids*, in ASME, Symposium on thermal properties (McGraw Hill Book Co., New York, N.Y., 1959).
- [8] W. H. Evans, T. R. Munson, and D. D. Wagman, *J. Research NBS* **55**, 147 (1955) RP2614.
- [9] D. D. Wagman and W. H. Evans, NBS (private communication).
- [10] W. D. Davis and G. Stegeman, *J. Am. Chem. Soc.* **71**, 2775 (1949).
- [11] J. Smisko and L. S. Mason, *J. Am. Chem. Soc.* **72**, 3679 (1950).
- [12] E. R. Van Artsdalen and K. P. Anderson, *J. Am. Chem. Soc.* **73**, 579 (1951).
- [13] E. Wichers, *J. Am. Chem. Soc.* **78**, 3235 (1956).
- [14] L. Troost and P. Hautefeuille, *Ann. chim. et phys.* [5] **9**, 70 (1876); *Compt. rend.* **70**, 185 (1870).
- [15] P. A. Favre and J. T. Silberman, *Ann. chim. et phys.* [3] **34**, 357 (1852); [3] **36**, 1 (1852); [3] **37**, 406 (1853).
- [16] M. Berthelot, *Thermochemie, II* (Gauthier-Villars et Fils, Paris, 1897); *Ann. chim. et phys.* [5] **15**, 185 (1878).
- [17] J. Thomsen, *Thermochemische Untersuchungen, I* (Verlag J. A. Barth, Leipzig, 1882).
- [18] A. W. Laubengayer and D. S. Sears, *J. Am. Chem. Soc.* **67**, 164 (1945).
- [19] A. F. Kapustinskii and O. Ya. Samoilov, *Izvest. Akad. Nauk. S.S.S.R. Otdel. Khim. Nauk.* 1952, 218; *Chem. Abstr.* **46**, 9406 (1952).
- [20] H. A. Skinner and N. B. Smith, *Trans. Faraday Soc.* **49**, 601 (1953).
- [21] J. R. Lacher, R. E. Scruby, and J. D. Park, *J. Am. Chem. Soc.* **74**, 5292 (1952).
- [22] C. C. Nathan, Thesis, University of Pittsburgh (1948).
- [23] W. A. Roth, E. Börger, and A. Bertram, *Ber* **70B**, 971 (1937).

WASHINGTON, January 21, 1959.

Important Notice

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