

# Heats of Formation of Aluminum Diboride and $\alpha$ -Aluminum Dodecaboride<sup>1</sup>

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The energies of combustion of  $\text{AlB}_2$  and  $\alpha\text{-AlB}_{12}$  were measured in a bomb calorimeter using fluorine as the oxidant. Major problems of this investigation were the assessment of the state and distribution of impurities in the samples and the establishment of the stoichiometry of the aluminum boride phase. We obtain  $-16 \pm 3$  kcal mol<sup>-1</sup> and  $-48 \pm 10$  kcal mol<sup>-1</sup> for the heats of formation of  $\text{AlB}_2$  and  $\alpha\text{-AlB}_{12}$ , respectively. The uncertainties cited are the overall experimental errors. Their magnitudes are chiefly due to uncertainties in the impurity correction applied and the uncertainties in the heats of formation of the combustion products.

Key Words: Aluminum diboride,  $\alpha$ -aluminum dodecaboride, aluminum fluoride, bomb calorimeter, boron trifluoride, fluorine, heat of combustion, heat of formation, Teflon.

## 1. Introduction

Thermodynamic data on the aluminum borides are not plentiful. There exist essentially no data from which the heats of formation can be calculated. Van Arkel [1]<sup>2</sup> estimated the heat of formation of aluminum diboride to be  $-80$  kcal mol<sup>-1</sup> by a method that he did not describe. The vapor pressure of  $\text{AlB}_{12}$  was measured by Bolgar, Verkhoglyadova, and Samsonov [2] between 1100 and 2000 °C. They observed aluminum in the vapor, but do not state whether any other species were present in the vapor. It is, therefore, not clear what relationship exists between their calculated heat of vaporization, and the heat of formation of  $\text{AlB}_{12}(c)$ . Interpretation of their work is further complicated by the discrepancy of about an order of magnitude in the heats of vaporization of titanium diboride and zirconium diboride as reported by the above authors and as reported by Schissel and Trulson [3] and by Leitnaker, Bowman, and Gilles [4].

Because no calorimetric study had been made to determine the heats of formation of any of the borides of aluminum, we undertook this task using fluorine bomb calorimetry. Combustion of the aluminum borides in oxygen presumably forms two solid oxides as products,  $\text{Al}_2\text{O}_3$  and  $\text{B}_2\text{O}_3$ , which may interact with one another, and may retain unburned starting material mixed with them. The amount of reaction is very difficult to determine in this kind of process. On the other hand, when an aluminum boride is burned in

fluorine one of the products is gaseous and the difficulties in obtaining a more complete reaction and of measuring the degree of completeness are correspondingly decreased.

A previous study of the combustion of aluminum [5, 6] in fluorine in our laboratory provided a directly applicable technique for carrying out the reaction process in the calorimeter, and in addition, provided some of the essential auxiliary data necessary to calculate the heat of formation of the aluminum borides from their heats of combustion in fluorine. Concurrently with this work a study of the combustion of boron in fluorine was carried out, and is reported elsewhere [7]. The determination of the heats of combustion of aluminum and boron in fluorine using the same calorimetric system and the same preparative technique for the samples was considered important in order to minimize systematic errors because relatively small heats of formation for the aluminum borides are to be deduced from large heats of combustion.

At the time this work was undertaken, no studies had been made of refractory borides using the fluorine bomb technique and a large fraction of our interest was in the establishment of techniques and in the formation of an appraisal of the ultimate usefulness of the technique chosen for refractory compounds. However, the lack of data on the aluminum borides in particular, and metallic borides in general, can also be linked to difficulties met in preparing and characterizing single phase materials having a definite stoichiometry and a high state of purity. Although the samples used were as good in quality as we considered to be obtainable at the time, we found that interpreting

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<sup>2</sup> Figures in brackets indicate the references at the end of this paper.

the type and distribution of impurities, normalizing the sample composition, and deciding upon the stoichiometry of the boride phase were more difficult than performing the heat measurements.

Calorimetric measurements were performed on samples of  $\text{AlB}_2$ ,  $\alpha\text{-AlB}_{12}$ , and  $\gamma\text{-AlB}_{12}$ . The measurements on  $\alpha\text{-AlB}_{12}$  were amenable to interpretation in terms of stoichiometry although the total observed analysis was found to be in excess of 100 percent. The measurements on  $\text{AlB}_2$  were more difficult to interpret because of the deviation of the apparent formula from stoichiometry, and greater deviation of the total observed analysis from 100 percent. We found it impossible to obtain a reasonable interpretation of the measurements on  $\gamma\text{-AlB}_{12}$  for the following reasons: the sample contained about 10 percent of the  $\alpha$ -phase syntactically intergrown, the apparent formula was calculated to be  $\text{AlB}_{12.57}$ , the total observed analysis was only 97.2 percent, and only two calorimetric measurements were made. Therefore, only the measurements on  $\text{AlB}_2$  and  $\alpha\text{-AlB}_{12}$  are reported here.

## 2. Materials

The aluminum borides were prepared for us by the Carborundum Company and are similar to materials described by Matkovich, Economy and Giese [8]. The elemental analysis for the aluminum borides is given in table 1. Unless otherwise indicated analyses were performed by the NBS Analysis and Purification Section. Analyses for aluminum, boron and metallic impurities did not differ significantly from those obtained by the supplier. Crystallographic examinations by x-ray diffraction were made by the NBS Crystallography Section.

The aluminum diboride sample consisted of extremely thin black crystalline platelets with areas up to several  $\text{mm}^2$ , having a metallic luster. Inspection of table 1 shows the boron content of the  $\text{AlB}_2$  sample to be in excess of the theoretical value. The observed boron to aluminum atomic ratio is 2.215 which is ascribed by the supplier to lattice vacancies and/or boron atoms in aluminum positions. The x-ray pattern showed the aluminum diboride sample to be hexagonal. The lattice constants found were,  $a = 3.005 \text{ \AA}$ , and  $c = 3.250 \text{ \AA}$ , in good agreement with previously reported constants for this phase ( $a = 3.009 \text{ \AA}$  and  $c = 3.262 \text{ \AA}$  [9]).

The  $\alpha\text{-AlB}_{12}$  sample was obtained as a reddish-brown powder having a maximum particle size of about  $75 \mu$ . The boron and aluminum analyses on this sample gave a boron to aluminum atomic ratio which was essentially stoichiometric, 12.03. X-ray analysis showed the unit cell to be tetragonal with the lattice constants,  $a = 10.162 \text{ \AA}$  and  $c = 14.26 \text{ \AA}$  (previously reported:  $a = 10.161 \text{ \AA}$  and  $c = 14.283 \text{ \AA}$  [10]).

The samples were analyzed for boron, aluminum, and metallic impurities using appropriate wet chemical and instrumental methods. Nitrogen in the samples was determined by the Kjeldahl method. Carbon was determined gravimetrically by oxygen

TABLE 1. *Elemental analysis of the aluminum borides (weight percent)*

Aluminum Boride	$\text{AlB}_2$	$\alpha\text{-AlB}_{12}$
Al theoretical.....	55.51	17.22
B theoretical.....	44.49	82.78
Al found.....	53.00	16.98
B found.....	47.04	81.85
Cu.....	0.075	
Fe.....	.025	
Si.....	.026	0.05
Mg.....	.024	.15
Ca.....	.013	.018
Mn.....	.010	
O.....	<sup>a</sup> (1.0), <sup>b</sup> 0.89	<sup>a</sup> (1.3), <sup>b</sup> 1.44
N.....	.30	0.27
C.....	.08	.11
Total.....	101.483	100.868

<sup>a</sup> Neutron activation analysis (General Atomic).

<sup>b</sup> Inert-gas fusion analysis (Ledoux and Co.).

(The inert-gas fusion results for oxygen were used in forming the totals.)

combustion of the sample and measurement of the  $\text{CO}_2$  formed. The oxygen content of the aluminum borides was determined by neutron activation and inert-gas fusion techniques. The oxygen analysis by inert-gas fusion is preferred over the analysis by neutron activation because of suspected interference of isotopic species produced from irradiation of the boron in the sample [11].

The Teflon (polytetrafluoroethylene) film and the Teflon powder ("Teflon 5") used in preparing pelleted mixtures, and the fluorine used in the heat measurements were the same as described in an earlier paper [6]. Neither the Teflon film nor powder was modified or treated in any special way prior to use. The energy of combustion,  $\Delta E_{303}^\circ$ , of "Teflon 5" was  $-10,371.7 \text{ Jg}^{-1}$ . The fluorine was analyzed using the mercury absorption technique [12] and found to be 99.79 percent  $\text{F}_2$ .

## 3. Treatment of the Analytical Data

Because of the large departure of the total elemental analysis of the aluminum borides from 100 percent, it has been a difficult task to decide upon how much of the aluminum boride was present and in what state the impurities occurred. The difficulty was aggravated by the nonstoichiometry evident in  $\text{AlB}_2$ . Whether  $\text{AlB}_2$  is nonstoichiometric as implied by the boron to aluminum ratio, or whether interaction of the impurities with boron and aluminum merely gives this impression, remains unsolved. Chemical analyses for constituent elements have shown that both  $\text{AlB}_2$  and  $\alpha\text{-AlB}_{12}$  samples possess total compositions of 101.5 and 100.9 percent, respectively. A gross error in the analysis of one or more elements is required in order to account for the discrepancy, but has not been found.

Summaries of the treatments of the impurities in aluminum diboride and  $\alpha$ -aluminum dodecaboride are shown in tables 2 and 3 in which five treatments are presented. In all cases we have assumed the metallic

TABLE 2. Treatment of Impurities in AIB<sub>2</sub>

Treatment	1	2	3	4	5
Normalization mode	Entire composition	Entire composition	Entire composition	Impurities only	AIB <sub>2</sub> content only
AIB <sub>2</sub>	90.848	94.078			
AIB <sub>2.215</sub>			97.409	98.854	97.371
Al					
B	5.937	3.593			
Cu	0.074	0.074	0.074	0.033	0.075
Fe	.025	.025	.025	.011	.025
Si	.026	.026	.026	.011	.026
Mg	.024	.024	.024	.010	.024
Ca	.013	.013	.013	.006	.013
Mn	.010	.010	.010	.004	.010
Al <sub>2</sub> O <sub>3</sub>	1.863		.579	.256	.588
B <sub>2</sub> O <sub>3</sub>		1.272	.876	.388	.889
AlN	0.866		.269	.119	.273
BN		0.524	.361	.160	.366
Al <sub>4</sub> C <sub>3</sub>	.315		.181	.080	.184
B <sub>4</sub> C		.363	.154	.068	.156
Total	100.001	100.002	100.001	100.000	100.000

TABLE 3. Treatment of impurities in  $\alpha$ -AIB<sub>12</sub>

Treatment	1	2	3	4	5
Normalization mode	Entire composition	Entire composition	Entire composition	Impurities only	$\alpha$ -AIB <sub>12</sub> content only
$\alpha$ -AIB <sub>12</sub>	83.564	96.521			
$\alpha$ -AIB <sub>12.03</sub>			96.653	97.492	96.624
Al		0.216			
B	11.969				
Mg	0.149	.149	0.149	0.111	0.150
Si	.050	.050	.050	.037	.050
Cu	.018	.018	.018	.013	.018
Al <sub>2</sub> O <sub>3</sub>	3.033		.233	.175	.235
B <sub>2</sub> O <sub>3</sub>		2.071	1.911	1.432	1.928
AlN	0.783		0.060	.045	.061
BN		0.474	.437	.328	.441
Al <sub>4</sub> C <sub>3</sub>	.435		.087	.065	.088
B <sub>4</sub> C		.502	.402	.301	.405
Total	100.001	100.001	100.000	99.999	100.000

impurities in AIB<sub>2</sub> and  $\alpha$ -AIB<sub>12</sub> to be present as the elements. When one considers the possible distribution of nonmetallic impurities, two possibilities present themselves. First, the aluminum boride can be considered as stoichiometric and the nonmetals as combined entirely with one element or the other. Some excess of elemental aluminum or boron will also be present. This gives two extreme cases which are shown in tables 2 and 3 in treatments marked (1) and (2). In treatment (1) the nonmetals are combined entirely with aluminum, leaving an excess of elemental boron, and in treatment (2) they are combined entirely with boron, leaving an excess of elemental aluminum. Second, the aluminum boride samples can be considered as nonstoichiometric and the nonmetallic impurities as distributed between boron and aluminum in proportion to the relative number of moles of boron and aluminum. This latter possibility appears to us to represent a more probable situation in the absence of specific information about the distribution of the elements.

In either case, since the total elemental analysis of AIB<sub>2</sub> and  $\alpha$ -AIB<sub>12</sub> deviates from 100 percent, we must normalize the composition in order to attain a proper mass balance. The mode of normalization used in

treatments 1, 2, and 3 of tables 2 and 3 is that involving the entire composition. Inherent in this procedure is the assumption that the error in a particular analysis for an element is proportional to the amount of that element present in the sample. This assumption introduces a large adjustment in the case of the boron analysis in our  $\alpha$ -AIB<sub>12</sub> sample since it is the element present in the greatest amount and also because the deviation of the total composition from 100 percent is large. Treatments (4) and (5) of tables 2 and 3 illustrate the effects of normalization in such ways as to throw the error completely into the boride phase, or into the impurities, and thus allow calculation of the extreme effects that the manner of treating the analysis can have on the calculated heat of formation. Under treatment (4) the amount of the impurities is adjusted retaining the original amounts of AIB<sub>2</sub> and  $\alpha$ -AIB<sub>12</sub> as found from the analysis after the non-metallic impurity distribution had been taken into account. Treatment (5) results from retaining the original amounts of impurities and adjusting the amount of the boride phase.

It is evident that an indefinite number of distributions other than the ones suggested are possible. Because of the manner of assigning the compositions used in the various treatments, we feel that the heats of formation derived for AIB<sub>2</sub> and  $\alpha$ -AIB<sub>12</sub> using these treatments represent both the extreme and the more likely values, and envelop values that could result from most other selections of the sample composition. Treatment (1) of table 3 in which all the nonmetallic impurities are assumed to be combined entirely with aluminum is not a likely situation for the  $\alpha$ -AIB<sub>12</sub> sample, although it depicts a limit to an impurity state and distribution. Since boron comprises over 80 percent of the sample, it seems improbable that the non-metals would not interact with the boron. A smaller error may result from use of treatment (2) in which all of the nonmetals are assumed to combine with boron. In the case of the AIB<sub>2</sub> sample, treatments (1) and (2) seem more nearly equally likely since the weight percent of boron and aluminum is almost the same.

Several studies have shown that boron has a tendency to form interstitial compounds with certain light (low atomic weight) elements [13, 14]. These findings might possibly question certain choices for the distribution of nonmetals present in our samples between aluminum and boron. For example, when oxygen is present only in small proportions the oxygen combination with boron is likely to resemble B<sub>6</sub>O [14, 15] more than B<sub>2</sub>O<sub>3</sub>, however, no thermodynamic data are available on B<sub>6</sub>O to permit calculation with it as a possible impurity. In the absence of data on the binding of oxygen in a large excess of boron, we are forced to assume that the binding energy per oxygen atom is similar to that in B<sub>2</sub>O<sub>3</sub>. Interestingly enough,  $\alpha$ -AIB<sub>12</sub> may be considered an interstitial compound of aluminum in boron in view of recent work on the structure of  $\beta$ -rhombohedral boron [16, 17].

Treatment (3) of tables 2 and 3 is the most likely state and distribution for the impurities in that it

not only includes the interaction of the nonmetals with boron, but does not exclude such interaction with aluminum. Treatment (4) of tables 2 and 3 is not a likely representation of the sample composition because a range of values greater than 0.5 percent has been found in the determination of boron in the aluminum borides we have submitted for analysis, hence, giving the determination a high uncertainty. There is a striking similarity between treatments (3) and (5) which illustrates that our choice of the most likely distribution leans heavily upon the accuracy of the analyses of the impurities. It is also in keeping with our suspicions about the accuracy of boron analysis in refractory boron compounds. The effects of the impurity distribution and normalization made upon the calculation of the heats of formation of  $\text{AlB}_2$  and  $\alpha\text{-AlB}_{12}$  will be discussed in section 9.2.

#### 4. Preparation of Sample Pellets

Attempts to prepare suitable pellets of the aluminum borides under study, without the aid of an auxiliary substance, were not successful because of their hardness and resistance to compression, or their reaction with fluorine in the combustion bomb prior to the desired time of ignition. Three methods of sample preparation were used in preparing the samples for combustion in fluorine, which have already been described in detail earlier [5, 6]. In brief,

one method (Method A) consisted of weighing the sample powder and Teflon powder in a sealable Teflon bag, mixing the powder to obtain homogeneity, and pressing the mixture into pellet form. Another method (Method B) was used for samples which reacted with fluorine upon contact. An additional coating of Teflon was provided to prevent reaction from occurring. In a third technique (Method C), the sample powder and Teflon powder were weighed in a small beaker, mixed to obtain homogeneity and transferred to a pellet die for pressing. This latter method, which was the first method developed, was found to be not suitable for samples that reacted spontaneously with fluorine and was less satisfactory than Method A with respect to the accounting for weight losses. We assumed that the total loss of mixture took place in proportion to the amounts of sample and Teflon present in the pellet.

In table 4, we present a brief summary of the average quantities of sample and Teflon powder which comprise a prepared pellet of a given aluminum boride. Also included are the method used to prepare a pellet, the number of the experiment using a particular method, and losses encountered in preparing a pellet. Samples were weighed to the nearest 0.01 mg. The densities of the substances, used in making buoyancy corrections were as follows in  $\text{g cm}^{-3}$ : "Teflon 5", 2.23; Teflon film, 2.15;  $\text{AlB}_2$ , 2.955 [8];  $\alpha\text{-AlB}_{12}$ , 2.557 [10].

TABLE 4. Summary of the preparative technique used in the fluorine combustion of the aluminum borides

Sample in pellet	Method of preparation and experiment number using a given method	Mass Teflon bag	Mass sample in mixture	Mass Teflon in mixture	Mass Teflon coating	Loss Teflon in sealing bag (Methods A and B)	Mass mixture adhering to breaker (Method C)	Loss of mixture in pelleting	Total loss
		Grams	Grams	Grams	Grams	mg	mg	mg	mg
$\text{AlB}_2$	B 1-6	0.3	0.238	1.84	0.8	0.04	.....	0.22	0.26
$\alpha\text{-AlB}_{12}$	C 1-9	.....	0.312	1.77	.....	.....	0.33	0.26	0.59
	A 10	0.3	0.238	2.28	.....	0.16	.....	0.15	0.31
	B 11	0.3	0.200	1.70	0.8	0.02	.....	0.37	0.39

#### 5. Calorimetric System

No major changes had been made in the bomb calorimeter, heat measurement station or combustion bomb since our earlier work [6, 7] which was carried out in the same apparatus. The apparatus will be discussed here only briefly.

An isothermal-jacket, stirred-water calorimeter was used in making the heat measurements. The jacket was maintained at a constant temperature near 30 °C to within 0.002 °C. Temperature changes were measured to 0.0001 °C with a G-2 Mueller Bridge in conjunction with a platinum resistance thermometer. Reactions were carried out in an "A"-nickel combustion bomb (volume, 360  $\text{cm}^3$ ) designed for service with fluorine.

The quantities of the sample and Teflon powder in the pellet were adjusted to provide a temperature

rise of three degrees (27 to 30 °C). Two aluminum electrodes, each suspended from the bomb head by a Monel rod, held a tungsten fuse. Depending upon the diameter of the fuse an energy of either 20 J or 50 J was produced as a result of ignition and reaction of the fuse with fluorine. The electrical energy from the ignition process was assumed to be negligible. For procedures dealing with the loading and emptying of the combustion bomb, and for details of the design and construction of the fluorine manifold, our earlier work should be consulted [5].

#### 6. Products of Combustion

The white powder present in the combustion bomb as a result of burning the aluminum borides in fluorine was identified by its x-ray diffraction pattern as aluminum trifluoride. Previous work [5,6] has estab-

lished that Teflon burns in 15 to 20 atm of fluorine to carbon tetrafluoride as the only major product. Higher fluorocarbons were not detected in amounts greater than 0.02 mole percent. Product gases from the combustion of the aluminum borides in fluorine were analyzed in a mass spectrometer after absorption of the excess fluorine in mercury. Mass spectra comparable to those found in our earlier work [6, 7] were obtained. As in our work on the combustion of boron in fluorine, we found no sign of  $\text{BF}_3$  as a result of examination in a mass spectrometer. An interaction of some kind on the part of  $\text{BF}_3$  with the mercury fluoride formed during the absorption of fluorine is suspected.

Boron trifluoride was identified as a combustion product in an infrared spectrometer. Samples from aluminum boride-Teflon combustion experiments were examined in the region 400 to 600  $\text{cm}^{-1}$ , and the  $\text{BF}_3$  band at 481  $\text{cm}^{-1}$  was observed. Also present in the spectra was the  $\text{CF}_4$  band at 630  $\text{cm}^{-1}$ . Spectra of the evacuated cell and of  $\text{BF}_3$  alone were taken in this region in order to substantiate the identification. The cell used was 8 cm long and had polyethylene windows 0.0625 in thick.

## 7. Calibration Experiments

Twenty calibration experiments were performed in which benzoic acid (Standard Sample 39i) was burned in 30 atm of oxygen and with one ml of distilled water in the nickel combustion bomb. Their consistency and reproducibility have been discussed in our earlier paper [6]. The average energy equivalent was calculated to be  $14,803.27 \pm 0.99 \text{ J deg}^{-1}$ . The uncertainty cited is the standard deviation of the mean. The energy equivalent is that of the standard initial oxygen calorimeter which included the nickel combustion bomb with 30 atm of oxygen, a platinum crucible and fuse support wires, platinum fuse (2 cm long, 0.01 cm diam), a type 304 stainless-steel liner, Monel pellet holder, and no sample. Fastened to the bomb was a heater and ignition leads. The mass of the calorimeter vessel and water was 3750.0 g. The calorimetric data obtained in the calibration experiments were programmed for the IBM 7094

computer according to the procedures outlined by Shomate [18].

Using the appropriate heat capacity data, the energy equivalent of the standard oxygen calorimeter was adjusted to the proper value for the fluorine experiments. This involved allowing for the heat capacities of 30 atm of oxygen, 1 ml of distilled water, the platinum ware, 21 atm of fluorine and two aluminum electrodes. The application of these corrections gave  $14,805.17 \text{ J deg}^{-1}$  for the energy equivalent of the standard initial fluorine calorimeter for the temperature range used.

## 8. Fluorine Combustion Experiments

The heat measurements on the aluminum borides were made contemporaneously with ten experiments, previously reported in detail [6], in which "Teflon 5" was burned in 21 atm of fluorine. The value listed in section 2 for the energy of combustion,  $\Delta E_{303}^\circ$ , was determined in these ten experiments.

Preliminary experiments on  $\text{AlB}_2$  in which Method C was used to prepare pelleted mixtures showed a slow reaction with fluorine in the fore-period of the experiment, i.e., prior to the time of ignition. Six heat measurements, shown in table 5, were performed in which  $\text{AlB}_2$ -Teflon pellets prepared by Method B were burned in 21 atm of fluorine. Normal values for the fore-period drift rates and the apparent heat transfer coefficients were observed, indicating the absence of a premature reaction.

Eleven heat measurements shown in table 6, were made in which  $\alpha\text{-AlB}_{12}$ -Teflon pellets were burned in fluorine. In the first nine experiments a pressure of 16 atm of fluorine was used for combustion of a pelleted mixture prepared using Method C, which was the only method that had been developed in the early stages of this work. In the last two experiments on  $\alpha\text{-AlB}_{12}$ , which were made near the end of the work, a pressure of 21 atm of fluorine was used and the pellets were prepared by Methods A and B, respectively. No significant difference was observed in the heat measurements as a result of using different preparative techniques for the samples.

No sign of premature reaction was observed in experiments on  $\alpha\text{-AlB}_{12}$  as a result of inspecting the

TABLE 5. Aluminum diboride-Teflon combustion experiments

Experiment No.	1	2	3	4	5	6
(1a) $m(\text{AlB}_2 \text{ sample})$ .....gram...	0.267374	0.253674	0.220437	0.222195	0.226260	0.234477
(1b) $m(\text{Teflon})$ .....gram...	2.999471	2.846011	2.897229	2.957633	2.875395	2.933704
(2) $P(\text{F}_2)$ .....atm...	21.9	21.8	21.5	21.6	21.5	21.7
(3) $(e)$ ..... $\text{J deg}^{-1}$ ...	14,805.63	14,805.88	14,803.19	14,803.25	14,803.30	14,801.49
(4) $\Delta t_c$ .....deg...	3.48196	3.29846	3.16402	3.21878	3.18094	3.26692
(5) $(e) - (\Delta t_c)$ ..... $\text{J}^{-1}$ ...	-51,552.6	-48,830.0	-46,837.6	-47,648.4	-47,088.4	-48,355.3
(6) $\Delta E$ fuse..... $\text{J}^{-1}$ ...	20.4	20.4	20.4	20.4	20.4	20.4
(7) $\Delta E$ gas..... $\text{J}^{-1}$ ...	11.8	11.0	11.4	11.5	11.2	11.5
(8) $\Delta E^\circ$ (Teflon)..... $\text{J}^{-1}$ ...	31,109.6	29,518.0	30,049.2	30,675.7	29,822.7	30,427.5
(9) $\Delta E_{303}^\circ$ ( $\text{AlB}_2$ sample)..... $\text{J g}^{-1}$ ...	-76,338.0	-76,005.4	-76,015.4	-76,242.9	-76,169.5	-76,322.6
(10) $\Delta E_{303}^\circ$ ( $\text{AlB}_2$ sample) = -76,182.3 $\text{J g}^{-1}$ .						
(11) Standard Deviation of the Mean = 59.7 $\text{J g}^{-1}$ = 0.73 $\text{kcal mol}^{-1}$ .						
(12) $\Delta E_{298}^\circ - \Delta E_{303}^\circ = -0.7 \text{ J g}^{-1}$ .						
(13) $\Delta E_{298}^\circ$ ( $\text{AlB}_2$ sample) = -76,183.0 $\text{J g}^{-1}$ .						

TABLE 6.  $\alpha$ -Aluminum dodecaboride-Teflon combustion experiments

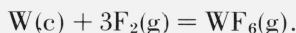
Experiment No.	1	2	3	4	5	6	7	8	9	10	11
(1a) $m(\alpha\text{-AlB}_{12}\text{ sample})$ .....g...	0.313053	0.319321	0.306651	0.311374	0.286230	0.305196	0.305665	0.345568	0.318994	0.200065	0.237862
(1b) $m(\text{Teflon})$ .....g.....	1.762627	1.759965	1.754308	1.763376	1.770452	1.771312	1.769831	1.784548	1.781811	2.724602	2.575942
(2) $P(\text{F}_2)$ .....atm.....	16.6	16.4	16.7	16.8	16.9	16.9	16.8	16.6	16.8	21.6	21.5
(3) $(\epsilon)$ .....J deg <sup>-1</sup> .....	14,804.37	14,804.41	14,804.21	14,804.29	14,805.19	14,804.42	14,804.42	14,803.41	14,804.11	14,799.95	14,803.61
(4) $\Delta t_c$ .....deg.....	3.20119	3.24529	3.15950	3.19296	3.04124	3.16284	3.16234	3.42228	3.25155	3.16372	3.29831
(5) $(\epsilon)(-\Delta t_c)$ .....J.....	-47,391.6	-48,044.6	-46,773.9	-47,269.5	-45,026.1	-46,824.0	-46,816.6	-50,661.4	-48,136.3	-46,822.9	-48,826.9
(6) $\Delta E_{\text{fuse}}$ .....J.....	41.7	37.4	37.5	36.9	36.2	31.8	42.1	42.0	42.5	20.4	20.4
(7) $\Delta E_{\text{gas}}$ .....J.....	6.5	6.4	6.4	6.5	6.6	6.6	6.3	6.6	6.6	12.6	11.9
(8) $\Delta E^\circ$ (Teflon).....J.....	18,281.4	18,253.8	18,195.2	18,289.2	18,362.6	18,371.5	18,356.2	18,508.8	18,480.4	28,258.8	26,716.9
(9) $\Delta E^\circ_{303}$ ( $\alpha\text{-AlB}_{12}$ sample).....J g <sup>-1</sup> .....	-92,834.1	-93,157.0	-93,053.0	-92,932.9	-93,004.6	-93,101.2	-92,951.4	-92,902.1	-92,813.0	-92,625.4	-92,817.3
(10) $\Delta E^\circ_{303}$ ( $\alpha\text{-AlB}_{12}$ sample)=-92,926.5 J g <sup>-1</sup> .											
(11) Standard deviation of the mean = 45.8 J g <sup>-1</sup> = 1.7 kcal mol <sup>-1</sup> .											
(12) $\Delta E^\circ_{298} - \Delta E^\circ_{303} = +0.9$ J g <sup>-1</sup> .											
(13) $\Delta E^\circ_{298}$ ( $\alpha\text{-AlB}_{12}$ sample)=-92,925.6 J g <sup>-1</sup> .											

fore-period drift rates and apparent heat transfer coefficients.

In each experiment the pelleted mixture was placed in the recess of a monel or "A"-nickel plate, the bomb was attached to the fluorine manifold and filled to the desired pressure. All bomb parts (bomb body, bomb head assembly and electrodes, liner and support plate) were weighed before the first experiment and after each experiment. Each part was washed with water and dried before the weighings were made.

The numbered entries in the tables are as follow:

- (1a) Mass of the sample mixed with Teflon in the pellet corrected for weight loss in preparation and for recovery of unburned sample.
- (1b) Mass of Teflon mixed with sample in the pellet corrected for weight loss.
- (2) Pressure of fluorine introduced into the bomb prior to combustion corrected to 30 °C.
- (3) Energy equivalent of the calorimeter for a given experiment.
- (4) Temperature change of the calorimeter thermometer corrected for heat of stirring and heat transfer.
- (5) Total energy change in the bomb process.
- (6) Energy liberated by the tungsten fuse assuming the fuse burns according to the reaction:



From the heat of formation of  $\text{WF}_6$  [19], we calculated 9.44 J mg<sup>-1</sup> for the energy of combustion of the fuse.

- (7) Net energy correction for the hypothetical compression and decompression of bomb gases.

$$\Delta E_{\text{gas}} = \Delta E^i(\text{gas})_0^{P_0(\text{gas})} + \Delta E^f(\text{gas})_0^{P_0(\text{gas})}.$$

- (8) Standard energy of combustion per gram of Teflon at 30 °C multiplied by the corrected mass of Teflon in the pellet.
- (9) Standard energy of combustion per gram of the sample.
- (10) Average standard energy of combustion per gram of the sample.

- (11) Standard deviation of the mean of the average cited in (10).

- (12) Heat capacity correction converting the reference temperature to 298 °K.

- (13) Standard energy of combustion of the sample at 298 °K not corrected for impurities.

The heat capacities at constant pressure,  $C_p$ , used in the calculation of entries (3) and (12) are as follows in cal deg<sup>-1</sup> g<sup>-1</sup> at 25 °C: aluminum, 0.216 [20]; boron, 0.245 [21]; Teflon, 0.28 [22];  $\text{AlB}_2$ , 0.23;  $\alpha\text{-AlB}_{12}$ , 0.24; aluminum fluoride, 0.213 [20]. The heat capacities of  $\text{AlB}_2$ , and  $\alpha\text{-AlB}_{12}$  were estimated by assuming the molar heat capacities of the compounds to be the sums of the atomic heat capacities of the elements. The heat capacities at constant volume,  $C_v$ , used in the calculation of entries (3) and (12) were 5.52 [23], 12.62 [24] and 10.04 [21] cal deg<sup>-1</sup> mol<sup>-1</sup>, respectively for fluorine, carbon tetrafluoride and boron trifluoride at 30 °C.

Washburn corrections, entry (7), were calculated following the procedure outlined by Hubbard [25] for experiments in which fluorine is used as the oxidant. The coefficients  $[\partial E/\partial P]_T = -T[dB/dT]$  were found in tables based on a Lennard-Jones 6-12 potential function as compiled by Hirschfelder, Curtiss, and Bird [26] using the appropriate force constants. The force constants used for fluorine, carbon tetrafluoride, and boron trifluoride were those determined by White, Hu, and Johnston [27], Douslin [28], and Brooks and Raw [29], respectively.

In calculating the corrections for the combustion of impurities in the  $\text{AlB}_2$  and  $\alpha\text{-AlB}_{12}$  samples, the following values, in kcal mol<sup>-1</sup>, were used for the heats of formation of other compounds:  $\text{Al}_2\text{O}_3$ , -400.4 [30];  $\text{B}_2\text{O}_3$ , -304.20 [31];  $\text{Al}_4\text{C}_3$ , -49.7 [32];  $\text{AlN}$ , -76.0 [20];  $\text{BN}$ , -60.8 [31];  $\text{MgF}_2$ , -268.7 [33];  $\text{CaF}_2$ , -290.3 [34];  $\text{SiF}_4$ , -385.98 [35];  $\text{FeF}_3$ , -235 [36];  $\text{CuF}_2$ , -126.5 [34];  $\text{MnF}_3$ , -238 [36]. In calculating the correction for the  $\text{B}_4\text{C}$  impurity in our samples, we have chosen  $\Delta E^\circ_{298} = -97.84$  kJ g<sup>-1</sup> for the reaction:  $\text{B}_4\text{C(c)} + 8\text{F}_2(\text{g}) = 4\text{BF}_3(\text{g}) + \text{CF}_4(\text{g})$  based upon heat measurements performed in our laboratory which will be reported in more detail in a future publication.

The combustion experiments were programmed for calculation in the same way as the calibration experi-

ments, however, the only valid data calculated by the computer were the corrected temperature rises,  $\Delta t_c$ , because the program used had not been modified to accommodate the use of fluorine as the oxidant.

Atomic weights were taken from the 1961 table of atomic weights based on  $C^{12}=12$  and adopted by the International Union of Pure and Applied Chemistry [37]. The unit of energy is the joule, and one calorie was defined as 4.1840 J.

## 9. Discussion and Results

### 9.1. Analysis of Combustion Residues

A residue assumed to be unburned Teflon and/or carbon was observed in heat measurements involving Teflon alone. No correction was applied to any experiment for this residue, and we assumed that the formation of the residue took place in all experiments approximately in proportion to the amount of Teflon initially present. The heat of combustion per gram of Teflon would, hence, be constant and the error due to residue formation would be eliminated when the energy due to the combustion of Teflon was subtracted from the total energy released in the combustion.

Aluminum fluoride residues resulting from the burning  $\alpha$ -AlB<sub>12</sub>-Teflon pellets prepared using Method C were analyzed for boron content in order to determine the amount of unreacted aluminum boride. In the analysis, the AlF<sub>3</sub> residue underwent carbonate fusion, followed by solution with acid and extraction of the aqueous phase with an organic solvent. The boron in the organic phase was determined spectrophotometrically with carminic acid [38]. The recovery of unburned  $\alpha$ -AlB<sub>12</sub> ranged from 0.01 to 0.04 mg.

Aluminum fluoride residues obtained from the combustion of AlB<sub>2</sub>-Teflon, and  $\alpha$ -AlB<sub>12</sub>-Teflon mixtures, in which Methods A and B were used for sample preparation were analyzed in the same way as the  $\alpha$ -AlB<sub>12</sub>-Teflon mixtures prepared by Method C except for the following differences. After fusion and acid solution, the boron in the aqueous phase was determined spectrophotometrically with methylene blue. The recovery ranged from 0.07 to 0.16 mg for AlB<sub>2</sub> and 0.34 to 0.41 mg for  $\alpha$ -AlB<sub>12</sub>.

A noncalorimetric experiment was performed in which an  $\alpha$ -AlB<sub>12</sub>-Teflon pellet was burned in 21 atm of fluorine and the AlF<sub>3</sub> residue was analyzed for carbon. Results of the analysis showed 0.17 mg of carbon present. A similar experiment was performed on an AlB<sub>2</sub>-Teflon pellet resulting in the detection of 0.33 mg of carbon in the AlF<sub>3</sub> residue. Both results are somewhat above the values found for carbon when Teflon burns alone in fluorine (0.05 to 0.15 mg [6]), however, no correction has been applied to the data for them.

### 9.2. The Heats of Formation of Aluminum Diboride and $\alpha$ -Aluminum Dodecaboride

Tables 7 and 8 show a range of calculated values for the heats of combustion and formation of our aluminum diboride and  $\alpha$ -aluminum dodecaboride samples and the dependence of these values upon the type of impurity correction applied. The datum in row 4 of these tables is the uncorrected energy of combustion obtained from the heat measurements shown in entry (13) of tables 5 and 6. The corrected energy of combustion is given in row 7 of the tables and is obtained by subtracting the energy contribution of the impurities (row 5) from row 4 and dividing by the fraction of the sample calculated to be the pure aluminum boride phase for a given treatment (row 6). The  $\Delta nRT$  term (row 8) allows for the calculation of the heats of combustion in  $Jg^{-1}$  (row 9) and  $kcal (gfw)^{-1}$  (row 10). The heat of formation per gram-formula-weight of the formula in row 2 for each treatment is calculated in row 11 by taking the difference between the sum of the heat of formation of the products (row 12) and the corresponding heat of combustion in row 10. The values used for the heats of formation of AlF<sub>3</sub>(c) and BF<sub>3</sub>(g) are  $-361.0 \pm 1.6$  and  $-271.03 \pm 0.51$  kcal mol<sup>-1</sup>, respectively, as determined from our earlier work [5, 6, 7]. The uncertainties cited are the overall experimental errors of the respective studies.

For the sake of consistency, the treatments shown in row 1 of tables 7 and 8 correspond with the respective treatments in tables 2 and 3 of section 3.

As mentioned earlier in section 3, the treatment of the impurities which seem most likely to be relevant appears in tables 7 and 8 as treatment 3. In this treatment the assumption is made that the non-

TABLE 7. The dependence of the heat data upon the treatment of the impurities in AlB<sub>2</sub>

1 Treatment.....	1	2	3	4	5
2 Stoichiometry.....	AlB <sub>2</sub>	AlB <sub>2</sub>	AlB <sub>2.215</sub>	AlB <sub>2.215</sub>	AlB <sub>2.215</sub>
3 Assumptions regarding the state and distribution of the impurities.....	Nonmetals combined entirely with aluminum; free boron present	Nonmetals combined entirely with boron; free aluminum present	Nonmetals distributed between aluminum and boron in proportion to the amount of aluminum and boron present in the sample.		
4 Energy of combustion, uncorrected for impurities (from table 5)..... $J g^{-1}$ ...	-76,183.0	-76,183.0	-76,183.0	-76,183.0	-76,183.0
5 Energy of combustion of impurities..... $J g^{-1}$ ...	-6,948.0	-4,529.9	-708.8	-312.7	-718.5
6 Fraction of sample calculated to be pure AlB <sub>2</sub> (or AlB <sub>2.215</sub> ).....	0.90848	0.94078	0.97409	0.98854	0.97371
7 Energy of combustion, corrected, $\Delta E_{298}^{\circ}$ ..... $J g^{-1}$ ...	-76,209.7	-76,163.5	-77,481.8	-76,749.9	-77,502.0
8 $\Delta nRT$ term..... $J g^{-1}$ ...	-127.5	-127.5	-137.4	-137.4	-137.4
9 Heat of combustion, $\Delta H_{298}^{\circ}$ ..... $J g^{-1}$ ...	-76,337.2	-76,291.0	-77,619.2	-76,887.3	-77,639.3
10 Heat of combustion, $\Delta H_{298}^{\circ}$ ..... $kcal (gfw)^{-1}$ ...	-886.77	-886.24	-944.78	-935.88	-945.03
11 Heat of formation, $\Delta H_{298}^{\circ}$ ..... $kcal (gfw)^{-1}$ ...	-16.29	-16.82	-16.55	-25.45	-16.30
12 Sum of the heats of formation of the products..... $kcal (gfw)^{-1}$ ...	-903.06	-903.06	-961.33	-961.33	-961.33

TABLE 8. The dependence of the heat data upon the treatment of the impurities in  $\alpha\text{-AlB}_{12}$ 

1	Treatment.....	1	2	3	4	5
2	Stoichiometry.....	$\alpha\text{-AlB}_{12}$	$\alpha\text{-AlB}_{12}$	$\alpha\text{-AlB}_{12.03}$	$\alpha\text{-AlB}_{12.03}$	$\alpha\text{-AlB}_{12.03}$
3	Assumptions regarding the state and distribution of the impurities.....	Nonmetals combined entirely with aluminum; free boron present	Nonmetals combined entirely with boron; free aluminum present	Nonmetals distributed between aluminum and boron in proportion to the amount of aluminum and boron present in the sample.		
4	Energy of combustion, uncorrected for impurities (from table 6).....	-92,925.6	-92,925.6	-92,925.6	-92,925.6	-92,925.6
5	Energy of combustion of impurities.....	-13,530.4	-1,178.8	-1,024.5	-767.4	-1,029.9
6	Fraction of sample calculated to be pure $\alpha\text{-AlB}_{12}$ (or $\alpha\text{-AlB}_{12.03}$ ).....	0.83564	0.96521	0.96653	0.97492	0.96624
7	Energy of combustion, corrected, $\Delta E_{298}^{\circ}$ .....	-95,012.3	-95,054.7	-95,084.5	-94,529.9	-95,104.3
8	$\Delta nRT$ term.....	-118.6	-118.6	-118.4	-118.4	-118.4
9	Heat of combustion, $\Delta H_{298}^{\circ}$ .....	-95,130.9	-95,172.3	-95,202.9	-94,648.3	-95,222.7
10	Heat of combustion, $\Delta H_{298}^{\circ}$ .....	-3563.2	-3564.7	-3573.2	-3552.4	-3574.0
11	Heat of formation, $\Delta H_{298}^{\circ}$ .....	-50.2	-48.7	-48.3	-69.1	-47.5
12	Sum of the heats of formation of the products.....	-3613.4	-3613.4	-3621.5	-3621.5	-3621.5

metals are distributed between aluminum and boron in proportion to the amount of aluminum and boron present in the sample. Also reasonably probable is treatment 5, in which the total amount of impurities is assumed to be correct and the normalization of the composition is made entirely by adjusting the amount of the aluminum boride phase.

Treatment (2) represents a probable situation for both  $\text{AlB}_2$  and  $\alpha\text{-AlB}_{12}$  while treatment (4) does not; treatment (1) represents a probable situation for  $\text{AlB}_2$  but not for  $\alpha\text{-AlB}_{12}$ . In treatments (3), (4), and (5), the heat of formation is calculated assuming the boride phase to be nonstoichiometric, however, an equivalent result is obtained if we assume the aluminum boride to be stoichiometric but accompanied by an excess of elemental boron. With the application of a correction for this excess, the calculation of the heats of formation of the stoichiometric and nonstoichiometric formulas become identical. Although certain treatments depict unlikely situations, they have been presented to show possible extremes in the calculations and to be used in estimating errors.

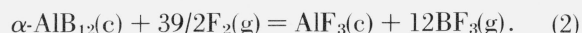
We have selected  $-16 \text{ kcal mol}^{-1}$  as the best value for the heat of formation of stoichiometric  $\text{AlB}_2$ . This value is the average of the calculated heats of formation found in treatments (1), (2), (3), and (5) of table 7. It will be noted that the calculation in treatments (1) and (2) gives results for the heat of formation of the stoichiometric formula,  $\text{AlB}_2$ , which shows little difference numerically from the calculation in treatments (3) and (5) for the heat of formation of the nonstoichiometric formula,  $\text{AlB}_{2.215}$ . Thus the value  $-16 \text{ kcal mol}^{-1}$ , could as readily be selected for the heat of formation of  $\text{AlB}_{2.215}$ .

In a similar manner, we have chosen  $-48 \text{ kcal mol}^{-1}$  as the best value for the heat of formation of stoichiometric  $\alpha\text{-AlB}_{12}$ . This value is the average treatments (2), (3), and (5) in table 8. Here again, these treatments give almost the same heat of formation regardless of the stoichiometry. In this case, the stoichiometric and nonstoichiometric formulas are close enough together to be of little concern.

In making these selections, the factors of stoichiometry, manner of normalization of the composition, and distribution of the nonmetallic impurities have been considered. It is of interest to note that

those methods of treatment which on an a priori basis appear to us to represent the more probable situations give values for the heats of formation which lie rather close together.

Assuming the borides to be stoichiometric, eqs (1) and (2) illustrate the combustion processes for  $\text{AlB}_2$  and  $\alpha\text{-AlB}_{12}$ :



We calculate the heats of combustion in fluorine of  $\text{AlB}_2$  and  $\alpha\text{-AlB}_{12}$  to be  $-887$  and  $-3565 \text{ kcal mol}^{-1}$ , respectively, on the basis of the selected values for the heats of formation of these borides.

### 9.3. Sources of Error

The error incurred as a result of deciding upon the appropriate impurity distribution, which in turn defines the amount of  $\text{AlB}_2$  in the sample, was  $2.2 \text{ kcal mol}^{-1}$ . We calculated this value by taking the difference between the corrected and uncorrected energies of combustion (rows 7 and 4 of table 7) and finding the average deviation of the differences. Using a similar approach, we calculated the error due to the choice of the appropriate impurity distribution for  $\alpha\text{-AlB}_{12}$  to be  $6.8 \text{ kcal mol}^{-1}$ . The errors introduced by the uncertainties in the heats of formation of  $\text{AlF}_3(\text{c})$ ,  $1.6 \text{ kcal mol}^{-1}$ , and  $\text{BF}_3(\text{g})$ ,  $0.51 \text{ kcal mol}^{-1}$ , were calculated to be  $1.9$  and  $6.3 \text{ kcal mol}^{-1}$  for the  $\text{AlB}_2$  and  $\alpha\text{-AlB}_{12}$  data, respectively. These values were obtained by taking the square root of the sum of the squares of the terms,  $(x)(1.6)$  and  $(y)(0.51)$ , in which  $x$  and  $y$  corresponding to the moles of  $\text{AlF}_3(\text{c})$  and  $\text{BF}_3(\text{g})$  formed in the combustion reaction. We estimate that the error introduced by the uncertainties in the heats of formation of the products is an upper limit because the measurements made on the heats of formation of  $\text{AlF}_3$  and  $\text{BF}_3$ , as well as the heat of combustion of  $\alpha\text{-AlB}_{12}$  in fluorine were performed using the same calorimetric system and were subject to the same preparative procedure for the samples. Hopefully, because of these features, certain systematic errors would tend to cancel. Errors incurred as a result of



performing the heat measurements, such as the error from calibration or combustion experiments, losses in sample preparation, analysis for the amount of unburned  $\alpha$ -AlB<sub>12</sub>, incomplete fuse combustion, etc., are adequately covered by using two times the standard deviation of the mean, (entry 11, tables 5 and 6). Finally, by taking the square root of the sum of the squares of the three main sources of error, we obtain 3 and 10 kcal mol<sup>-1</sup> for the estimated error of the heats of formation of AlB<sub>2</sub> and  $\alpha$ -AlB<sub>12</sub>, respectively.

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