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HEATS OF FORMATION OF METALLIC BORIDES BY FLUORINE BOMB CALORIMETRY

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FOREWORD

This report was prepared by the National Bureau of Standards under USAF Delivery Order Nr. 33(615)64-04, which was later changed to Delivery Order Nr. 33(615)64-1003, and Amendment Nr. 1(65-1438). The work was initiated under Project Nr. 3048 and Task Nr. 304802. The initiator and buyer were A. E. Zengel, APFL, and H. E. Richeson, SEKNB, respectively.

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The validity of the measurements and calculations made in this investigation was dependent upon the procurement of good quality samples. The aluminum borides and the boron carbide sample were obtained from the Carborundum Company on a cost sharing basis. The graphite sample was obtained from the Ultra Carbon Corporation, while the sample of crystalline boron was a gift from the Eagle-Picher Company. The whole hearted cooperation of these suppliers is acknowledged in their effort to prepare samples of as high a purity as possible in the light of current technology.

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This technical report has been reviewed and is approved.

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ABSTRACT

The purpose of this work was to provide heat of formation data on boron and intermetallic borides which are applicable to calculations involving the combustion of slurry fuels

The heats of formation of $BF_3(g)$, $CF_4(g)$, $B_4C(c)$, $A\ell B_{2.215}(c)$, α-$A\ell B_{12}(c)$ and γ-$A\ell B_{12}(c)$ were calculated from the heats of combustion of boron, graphite, $B_4C(c)$, $A\ell B_{2.215}(c)$, α-$A\ell B_{12}(c)$ and γ-$A\ell B_{12}(c)$ in fluorine at high pressures. The heat measurements were made in a bomb calorimeter. The samples were subjected to thorough analysis and careful characterization. Three different methods were used to prepare pelleted mixtures of the samples with Teflon powder for combustion. The completeness of combustion was determined by analysis of the unburned sample remaining in the bomb after an experiment.

The heats of combustion in fluorine at 298°K and the corresponding standard deviations of the means, in kcal $mole^{-1}$ are given as follows, along with the substances for which they were determined: crystalline boron, -271.82 ±0.15; graphite, -222.87 ±0.04; $B_4C(c)$, -1290.7 ±0.5; $A\ell B_{2.215}(c)$, -946.27 ±0.73; α-$A\ell B_{12}(c)$, -3560.7 ±1.7; γ-$A\ell B_{12}(c)$, -3583.1 ±0.3.

The standard heats of formation at 298°K and the estimated over-all accuracies, in kcal $mole^{-1}$, are as follows: $BF_3(g)$, -271.82 ±0.38; $CF_4(g)$, -222.87 ±0.13; $B_4C(c)$, -19.5 ±4.6; $A\ell B_{2.215}(c)$, -16.2 ±2.9; α-$A\ell B_{12}(c)$, -61.5 ±10.9; γ-$A\ell B_{12}(c)$, -39.1 ±13.1.

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1.0 Introduction

In order to make accurate thermodynamic calculations of slurry fuel formulations involving boron or intermetallic borides, the thermodynamic properties of these substances must be well known. The main goal of this program has been to provide heat of formation data on boron and intermetallic borides which will find application in calculating the combustion properties of slurry fuels. Further application of this data can be found in evaluating the stability of intermetallic compounds, interpreting phase diagrams of binary metal systems and in calculating heats of reaction in which these particular substances are involved.

The heats of combustion of the following substances were measured in elemental fluorine: boron, boron carbide, graphite, aluminum diboride, α-aluminum dodecaboride and γ-aluminum dodecaboride. Although data on aluminum diboride and α-aluminum dodecaboride have been reported to this sponsor earlier [1], new heat measurements and analytical data warranted a recalculation of their heats of combustion and formation.

The technique used for determining the heats of combustion, and formation, of these substances was fluorine bomb calorimetry. Previous work [2] on the combustion of aluminum in fluorine provided a directly applicable technique for studying boron and intermetallic borides, and also provided some essential data needed in calculating the heats of formation of the aluminum borides. Oxygen bomb calorimetry is not particularly suitable for determining the heats of combustion of boron, boron carbide or the aluminum borides because boric oxide, a combustion product, may not be formed as a single phase material. It not only exists in both crystalline and amorphous forms, but lower oxides of boron are known also [3,4,5] and their formation during combustion would be undesirable. The combustion of the aluminum borides in oxygen has the further complication of forming two non-volatile products, Al_2O_3 and B_2O_3. Not only must consideration be given to interactions such as heats of mixing or solution of these two products, but also the extrication of unburned starting material from an Al_2O_3-B_2O_3 mixture. Recent work [6] has shown that more than one phase of aluminum oxide can be formed during a bomb combustion, giving additional complications.

The heat of formation of boron trifluoride has been derived from the heats of solution of gaseous BF_3 in water [9,10,11] and the heat of solution of boric oxide in aqueous HF [12,13], giving an average value for ΔH°_{f298} of -270 ±2 kcal $mole^{-1}$. Wise, Margrave, Feder and Hubbard [14] determined the heat of formation of boron trifluoride to be -269.88 ±0.+9 kcal $mole^{-1}$ in a bomb calorimeter by direct combination. Recent work by Johnson, Feder and Hubbard [15], using a two-chapter combustion bomb shows $\Delta H^{\circ}_{f298}[BF_3(g)] = -271.65$ kcal $mole^{-1}$ from the direct combination of the elements.

Although it has been demonstrated [7,8] that graphite can be burned successfully in an oxygen bomb to give precise data, attempts to determine the heat of formation of carbon tetrafluoride by direct combination of the elements has not been as simple. Von Wartenburg and Schütte [77] calculated the heat of formation of CF_4 to be -162 ±2 kcal $mole^{-1}$ as a result of the direct combination of the elements. Ruff and Bretschneider [78] later pointed out that the presence of fluorocarbons in the product gases necessitates a correction which changes the latter value for CF_4 to -183.5 kcal $mole^{-1}$.

Scott et al. [16] and Good et al. [17] have determined the heat of combustion of Teflon in an oxygen bomb and have calculated the heat of formation of carbon tetrafluoride to be -218.3 kcal $mole^{-1}$. Similar, but more recent work by Cox, Gundry and Head [18] on the heats of combustion of docosafluorobicyclohexyl, and docosafluorobicyclohexyl-benzoic acid mixtures in oxygen has been made. With the aid of auxiliary data the heat of formation of carbon tetrafluoride has been calculated to be -218.56 kcal $mole^{-1}$ or -225.63 kcal $mole^{-1}$ depending upon whether values for the heat of formation of HF(aq) were used as recommended in NBS Circular 500 [29] or as determined by Cox and Harrop [17], respectively. Domalski and Armstrong [2] have calculated for $\Delta H^{\circ}_{f298}[CF_4(g)] = -221.8$ kcal $mole^{-1}$ from measurements on the heat of combustion of Teflon in fluorine and a reassessment of the heat of formation of Teflon. Jessup, McCoskey and Nelson [22] calculated the heat of formation of $CF_4(g)$ from the reaction of methane with fluorine and found -220.4 kcal $mole^{-1}$. Kirkbride and Davidson [23] and von Wartenberg et al. [24,25] calculated -218, -231 and -225 kcal $mole^{-1}$, respectively, for the heat of formation of $CF_4(g)$ from the following reaction:

$$CF_4(g) + 4K(g) = 4KF(c) + C(c) \qquad (1)$$

Vorob'ev and Skuratov [26] calculated for $CF_4(g)$, $\Delta H^{\circ}_{f298} = -219.2$ ±2.3 kcal $mole^{-1}$ from a reaction similar to reaction (1) except that sodium was used rather than potassium. Duus [27] calculated $\Delta H^{\circ}_{f298}[CF_4(g)] = -212.7$ kcal $mole^{-1}$ from measurements on the explosive decomposition, explosive hydrogenation, and oxygen combustion of $C_2F_4(g)$. Neugebauer and Margrave [28] studied the decomposition and hydrogenation of

$C_2F_4(g)$ and calculated for $\Delta H^\circ_{f298}[CF_4(g)]$, -217.1 kcal mole^{-1}. Work by Baibuz [20] on the explosion of CF_4, H_2, O_2 and CO mixtures has led to a calculation of heat of formation of $CF_4(g)$ of -220.1 ±1.4 kcal mole^{-1}. Corrections for certain heat losses were later made for this study by Baibuz and Medvedev [21] and upon recalculation they found $\Delta H^\circ_{f298}[CF_4(g)] = -220.6 \pm 1.4$ kcal mole^{-1}. There also exist many review articles and compilations in the literature which attempt to select a "best value" for the heat of formation of carbon tetrafluoride [29,30,31].

Revised data for the heats of formation of HF(g) and HF(aq) by Evans [32] has affected some of the heat of formation data on carbon tetrafluoride directly in that certain reactions under investigation involved HF(g) or HF(aq) as a product. We have recalculated the following heat of formation data for $CF_4(g)$ using the revised HF data; Good et al. and Scott et al., -220.9 kcal mole^{-1}; Jessup et al., -218.0 kcal mole^{-1}; Neugebauer and Margrave, -220.4 kcal mole^{-1}.

Smith, Dworkin and Van Artsdalen [33], using bomb calorimetric techniques, burned boron carbide in oxygen. From the heat of combustion of B_4C and the heats of formation of amorphous B_2O_3 and CO_2, they calculated -13.8 kcal mole^{-1} for the heat of formation of boron carbide. Inspection of their data showed that the degree of completeness of combustion was not large, ranging from 25 to 41 percent. It also revealed that when the amounts of B_2O_3 and CO_2 produced in the combustion was measured, a deficiency in the CO_2 content was observed. The authors assumed that some of the carbon in boron carbide failed to burn and remained behind as free carbon. In view of the fact that incompleteness of combustion and non-stoichiometry, requiring analysis of both B_2O_3 and CO_2 were present, the agreement of the heat measurements made was good, $\Delta H^\circ_{c298} = -683.8 \pm 2.2$ kcal mole^{-1}. A recalculation of the data of Smith et al. by Evans [34] gave $\Delta H^\circ_{f298}[B_4C(c)] = -12.2$ kcal mole^{-1} after a more recent value for the heat of formation of amorphous B_2O_3 is used.

Earlier values for the heat of formation of B_4C cited in the literature, 66.0 [35,36,37] and 48.12 [38,39] kcal mole^{-1} are considered unreliable because of the obscurity of the source and lack of information concerning experimental methods and calculations.

As far as the borides of aluminum are concerned, there exists essentially no data from which the heats of formation may be calculated. Van Arkel [40] estimated the heat of formation of aluminum diboride by a method he did not describe. The vapor pressure of AlB_{12} was measured by Bolgar, Verkhoglyadova and Samsonov [41] between 1100° and 2000°C. They observed aluminum in the vapor but do not state whether other species were present also. Therefore, the relationship between their heat of vaporization and the heat of formation is not clear. Interpretation is further complicated by a discrepancy of about an order of magnitude in the heats of vaporization of TiB_2 and ZrB_2 as reported by the above authors and as reported by Schissel and Trulson [42] and by Leitnaker, Bowman and Gilles [43].

2.0 Characterization of the Samples

2.1 Elemental Boron

A ten gram sample of -100 mesh crystals of high purity boron, β-rhombohedral phase, was received from the Eagle-Picher Company. It was prepared by the hydrogen reduction of boron tribromide on a substrate of zone refined boron, as described by Starks and Buford [44]. The supplier reported that emission spectrographic analysis showed 3 ppm. Si and 7 ppm. Cu. Carbon analysis supplied showed 500 ppm. carbon, having been analyzed by the method Kuo et al. [45].

The boron sample was sent to the NBS Analysis and Purification Section for spectrographic analysis for metallic impurities and their subsequent analysis. The latter analysis in conjunction with that of the supplier is summarized in Table 1. Oxygen analysis was performed by neutron activation analysis at General Atomic while the nitrogen content was determined using the Kjeldahl technique at the National Bureau of Standards.

X-ray analysis on the boron sample by the NBS Crystallography Section showed good agreement with data reported earlier for lattice parameters [46]. The sample has lattice parameters of $a = 10.93$Å and $c = 23.95$Å, with a space group assignment of $R\bar{3}m$.

2.2 Boron Carbide

A 46.3 gram sample of boron carbide, having a particle size of -100 mesh was obtained from the Carborundum Company. The sample was analyzed by the NBS Analysis and Purification Section and the results presented in Table 2 along with the supplier's analysis. The nitrogen content in the boron carbide was determined at NBS by the Kjeldahl method while oxygen analysis was done at General Atomic by neutron activation analysis. The large dispersion of boron and carbon analysis determined at NBS and Carborundum are not easily reconciled. The range of analytical determinations varies from 0.1 percent to 2.7 percent for boron and from 0.25 percent to 1.2 percent for carbon. The extreme refractory nature of boron carbide and its resistance toward fusion and solution are, no doubt, influential factors. Using average values for the boron and carbon analyses, 77.85 percent boron and 20.32 percent carbon, gives a boron

Table 1

Analysis of Elemental Boron

Element	Composition (percent by weight)			
	Supplier's Analysis		NBS Analysis	
	Spect. Anal.	Quant. Anal.	Spect. Anal.	Quant. Anal.
Al	-		0.001-0.01	< 0.001
Fe	-		0.001-0.01	0.079
Mg	-		0.0001-0.001	0.002
Mn	-		0.001-0.01	0.014
Sr	-		0.001-0.01	0.002
Ca	-		0.01 -0.1	0.010
Cu	0.0007		0.0001-0.001	-
Ba	-		0.001-0.01	-
Si	0.0003		0.01 -0.1	0.012
N		-		< 0.005
O		-		0.161 (a)
C		0.05		0.11
Total Imp.	0.051		0.396	
% Boron	99.949		99.604	

(a) General Atomic, San Diego, California

Table 2

Analysis of Boron Carbide

Element	Composition (percent by weight)				
	Supplier's Analysis		NBS Analysis		
	Spect. Anal.	Quant. Anal.	Spect. Anal.	Spect. Anal.	Quant. Anal.
B(78.26%)[b]		79.28			76.6, 77.8, 77.7
C(21.74%)[b]		20.55			20.8, 19.6
Al	0.005		0.001-0.01	0.01-0.1	
Ba	-		-	0.001-0.01	
Ca	0.004		0.0001-0.001	0.01-0.1	
Cu	< 0.001		< 0.0001	0.001-0.01	
Fe	0.008		0.001-0.01	0.01-0.1	
Mg	< 0.001		0.0001-0.001	0.0001-0.001	
Mn	< 0.001		-	0.0001-0.001	
Ni	-		-	0.001-0.01	
Si	0.02		0.001-0.01	0.01-0.1	0.023
Zr	0.004		0.001-0.01	0.001-0.01	
Ti	< 0.001		-	-	
N		-			0.21
O		-			0.185[a]
% B_4C	99.874		97.742 *		

[a] General Atomic, San Diego, California

[b] Theoretical for B_4C

* This value for B_4C (97.742%) was obtained by summing the latest analytical values for boron and carbon, 77.7% and 19.6%, the NBS silicon analysis, the oxygen and nitrogen analyses, and using the Carborundum Co. analyses for the remaining metallic impurities.

to carbon ratio of 4.26. If one chooses the latest analytical results for boron and carbon, namely 77.7 and 19.6 percent, a boron to carbon ratio of 4.40 is obtained. In view of the large dispersion of the boron and carbon analyses and the poor mass balance of the total composition, we have chosen the stoichiometry $B_{4.00}C$ to represent the formula weight of our sample.

The sample was examined using X-ray techniques by the NBS Crystallography Section and found to be in good agreement with the established pattern for boron carbide. Similarly, the calculated lattice parameters, a = 5.559Å and c = 12.07Å, were found to agree well with the literature values [50].

2.3 Graphite

A four ounce (113 gram) sample of spectroscopic graphite powder was purchased from the Ultra Carbon Corporation having a particle size of -35 on 100 mesh and a total ash content specified as not exceeding ten ppm. No significant metallic impurities were found in the sample as a result of analysis by the NBS Analysis and Purification Section. Oxygen and nitrogen impurities were detected in the sample using neutron activation analysis (General Atomic) to be <86 ppm. and <204 ppm., respectively. The graphite sample underwent X-ray analysis by the NBS Crystallography Section. Lattice parameters were calculated to be, a = 2.462Å and c = 6.722Å, in good agreement with literature values [47,48,49].

2.4 Aluminum Diboride

The characterization of aluminum diboride has been adequately described in previous work [1]. No additional analyses were performed on this sample during the period of the present delivery order.

2.5 Aluminum Dodecaborides

Both α- and γ-aluminum dodecaboride are described in previous work [1] with respect to spectrographic, X-ray radiochemical and wet chemical analysis. Under the present delivery order both α-AlB_{12} and γ-AlB_{12} were analyzed at NBS for nitrogen by the Kjeldahl technique and were found to contain 0.27 and 0.02 percent nitrogen by weight, respectively. This nitrogen analysis is preferred to that performed by neutron activation methods in that the latter is not as sensitive below 0.3 percent in the presence of small amounts of other metallic impurities. Inclusion of the nitrogen analysis brings the total composition of α-AlB_{12} and γ-AlB_{12} to 100.408 and 97.290 percent by weight, respectively.

2.6 Teflon Powder and Film

Two Teflon powders were used in preparing mixtures for the combustion experiments and were designated as TFE Fluorocarbon Resins "Teflon 5" and Teflon 7", respectively. Both powders were composed of irregularly shaped particles which easily adhered to one another. "Teflon 5" particles ranged in size from 50 to 800 microns while those of "Teflon 7" were from 10 to 500 microns. The Teflon film used in preparing bags to hold powdered mixtures was designated as FEP Fluorocarbon film, type A, and has a thickness of 0.001 inch. The "Teflon 5" powder was used exclusively for heat measurements on the aluminum borides while "Teflon 7" was used in heat measurements on boron, boron carbide and graphite. Neither the powders nor the film were modified or treated in any special way prior to use.

2.7 Fluorine

The fluorine used in the heat measurements was a specially prepared high-purity commercial grade. The fluorine used for heat measurements on the aluminum borides and graphite had an average assay of 99.79 percent while that used for experiments on boron and boron carbide had an assay of 99.40 percent. The fluorine was analyzed by absorption in mercury and observing the pressure of the residual gases [51]. The volatile residue was examined in a mass spectrometer. Typical results are shown in Table 3 for the composition of the residues.

Table 3

Analysis of Fluorine Impurities (Mole Percent)

F_2 Assay	99.40	99.79
O_2	16.0	60.8
N_2	46.4	27.8
CO_2	2.91	5.07
CF_4	32.7	4.92
Ar	1.38	0.13
SO_2F_2	0.014	0.44
SiF_4	0.052	0.14
C_2F_6	0.38	0.31
SF_6	0.02	0.047
C_4F_8	0.41	0.23
C_3F_8	0.075	0.067
C_2F_4 or cyclic C_4F_8	0.006	0.027

3.0 Preparation of Sample Pellets

Attempts to prepare suitable pellets of the substances under study without the aid of an auxiliary substance were not successful because of the hardness and resistance to compression of some of the samples, 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, all of which use powdered Teflon as an auxiliary binding material.

Method I. The sample powder and Teflon powder were weighed in a 20 ml. beaker, mixed to obtain reasonable homogeneity, and transferred to a pellet die for pressing. Upon weighing the pelleted mixture, a loss of weight was always observed. The loss occurred from incomplete transfer of the mixture from the beaker to the die pieces, and adherence of the mixture to the die pieces as a result of the pelleting operation. The weighable quantity of lost mixture for the latter two operations was usually inadequate to account fully for the total loss of mixture. We assumed that the total losss of mixture took place in proportion to the amounts of Teflon and sample present in the pellet.

Method II [52] A thermoplastic Teflon bag was prepared from a piece of film (2.5 in. x 3.0 in. x 0.001 in.) by folding it over once and sealing two sides. The bag was placed in a 20 ml. beaker and the sample powder and Teflon powder were weighed consecutively inside the bag. The remaining open end of the bag was sealed and the sample and Teflon mixed. Care was taken not to exclude air from inside the bag before the final seal was made, since it facilitated the mixing operation. Be wearing a pair of 0.001 in. thick polyethylene gloves, the sealed bag could be passed from hand to hand to carry out the mixing of the two powders. The bag was placed in a pellet die, pierced with a needle in order to allow the air to escape and the pellet pressed. Losses were observed in the sealing operation and assumed to be Teflon exclusively. In the pelleting of the bagged mixture, we assumed the losses to take place in proportion to the amounts of each constituent in the pellet.

Method III. The sample powder was prepared in pellet form by mixing with Teflon powder in a Teflon bag as in Method II, except the die pieces used to press the pellet were smaller (0.625 in. diam.) as compared to those used in the previous pelleting techniques (0.75 in. diam.). The smaller pellet was then placed inside the larger pellet die on a thin layer of packed Teflon powder. Using a stainless steel tube of appropriate wall thickness, additional Teflon powder was packed in the space between the pellet and wall of the die piece. A final top layer of Teflon powder was packed over the pellet, and the contents pressed, giving a coating of Teflon around the smaller pelleted mixture.

Preliminary experiments showed that the addition of a Teflon coating around a pelleted mixture appeared to prevent either spontaneous combustion of the sample during loading of the bomb with fluorine or premature reaction of the sample prior to the desired ignition.

In Table 4, one finds a brief analysis of the quantities of Teflon and sample which comprise a prepared pellet for a given sample. Also included is the method used to prepare a pellet, the number of experiments involved, the losses encountered in preparing a pellet, and the type of support upon which the pellet lay.

In the boron, boron carbide, AlB_2, α-AlB_{12}, γ-AlB_{12}, and some of the graphite heat measurements, the "A" nickel plate used was 2 in. in diameter and 0.125 in. thick. The monel plate used in the AlB_2 and α-AlB_{12} work was 2.5 in. in diameter and 0.125 in. thick with an annular section cut out to retard heat conduction from the reaction zone. The variations of "A" nickel plate and/or calcium fluoride plate used in the graphite combustion experiments are numerous and will be discussed in detail in Section 8.

Use of the bag technique employed in Methods II and III is of definite advantage over Method I. Sample loss from the mixture remaining in the beaker after each transfer and loss in transferring the mixture to the pellet die are eliminated. This can be observed in the preparation of α-AlB_{12}-Teflon pellets and most strikingly with AlB_2-Teflon pellets. In the preparation of AlB_2-Teflon pellets using Method I, transfer of the mixture to the pellet die was hindered by the electrostatic attraction of AlB_2 crystals for the inner beaker surfaces. Hence, the mixture remaining in the beaker after transfer was to the best of our observations, AlB_2, and was treated as such in the treatment of sample losses.

Samples were weighed to the nearest 0.01 mg.

The densities of the Teflon film and powders were determined as part of this investigation. The Teflon film had a density of 2.15 g cm^{-3}, and the powders, "Teflon 5" and "Teflon 7" were 2.23 g cm^{-3} and 2.16 g cm^{-3}, respectively. The densities of the various samples studied were as follows: boron, 2.33 g cm^{-3} [53,54]; boron carbide, 2.52 g cm^{-3} [55]; graphite, 2.26 g cm^{-3} [56]; aluminum diboride, 2.955 g cm^{-3} [57]; α-aluminum dodecaboride, 2.557 g cm^{-3} [58] and γ-aluminum dodecaboride, 2.577 g cm^{-3} [58].

Table 4

Relation of Samples to Preparative Technique and Support Plate

Sample in Pellet	Method of Preparation and No. of Experiments per method	Mass Teflon Bag grams	Mass Sample in Mixture grams	Mass Teflon in Mixture grams	Mass Teflon Coating grams	Mass Mixture adhering to beaker (Method I) grams	Loss Teflon in Sealing Bag (Methods II and III) mg	Loss of Mixture in Pelleting mg	Total Loss mg	Type of Pellet Support Plate used in Combustion
Boron	III-10	0.3	0.155	1.88	0.7	–	0.32	0.30	0.62	"A" nickel
Boron Carbide	III-8	0.3	0.181	1.90	0.7	–	0.21	0.20	0.41	"A" nickel
Graphite	II-2	0.3	0.255	2.24	–	–	0.20	0.08	0.28	"A" nickel and CaF_2
	III-5	0.3	0.255	1.30	0.8	–	0.13	0.22	0.35	
$A\ell B_2$	I-5	–	0.314	1.97	–	4.93	–	0.53	5.46	monel
	III-6	0.3	0.238	1.84	0.8	–	0.04	0.22	0.26	"A" nickel
α-$A\ell B_{12}$	I-9	–	0.312	1.77	–	0.33	–	0.26	0.59	monel
	II-1	0.3	0.238	2.28	–	–	0.16	0.15	0.31	"A" nickel
	III-1	0.3	0.200	1.70	0.8	–	0.02	0.37	0.39	
γ-$A\ell B_{12}$	II-2	0.3	0.207	2.49	–	–	0.06	0.06	0.12	"A" nickel

4.0 Calorimetric Apparatus

No major changes were made in the calorimeter, heat measurement station or combustion bomb since the earlier work on $A\ell B_2$ and α-$A\ell B_{12}$. These apparatuses will be discussed here briefly, however, but for a detailed description the reader is referred to reference [1].

An isothermal-jacket, stirred-water calorimeter was used in making the heat measurements. The jacket was maintained isothermal near 30°C by an electronic thermoregulator. Temperatures were measured with a G-2 Mueller Bridge in conjunction with a platinum resistance thermometer to 0.0001°C. Reactions were carried out in an "A" nickel combustion bomb suitably designed for service with fluorine, having a volume of approximately 380 ml. Two aluminum electrodes, suspended from the bomb head by two monel rods, held a tungsten fuse. The fuse was about 5 cm in length and was either of 0.002 in. or 0.003 in. diameter, contributing about 20 J or 40 J, respectively, to the combustion energy. A heater was used in both calibration and combustion experiments to bring the calorimeter to the desired starting temperature.

For procedures dealing with the loading and emptying of the combustion bomb and for details concerning the design and construction of the fluorine manifold, our earlier work [1] should be consulted.

5.0 Products of Combustion

The white powder present in the combustion bomb as a result of burning $A\ell B_2$, α-$A\ell B_{12}$ and γ-$A\ell B_{12}$ in fluorine was identified by X-ray techniques as aluminum fluoride. Previous work [2] has established 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 0.05 mole percent. The product gases were analyzed in a mass spectrometer after absorption of the excess fluorine in mercury. Comparable mass spectra were obtained when Teflon, boron-Teflon, boron carbide-Teflon, graphite-Teflon, $A\ell B_2$-Teflon, α-$A\ell B_{12}$-Teflon and γ-$A\ell B_{12}$-Teflon mixtures were burned in fluorine. It was interesting to note that in reactions which produce boron trifluoride as a combustion product, no BF_3 was found in the mass spectroscopic analysis of product gases. It is suspected that under conditions of the reaction of fluorine with mercury, an interaction of some kind takes place between BF_3 and the mercury fluoride formed during the absorption of fluorine.

Boron trifluoride was identified as a combustion product by infrared spectroscopy. Samples from aluminum boride-Teflon, boron-Teflon, and boron carbide-Teflon combustions were examined in the region 650 to 400 cm^{-1}, and the BF_3 band at 481 cm^{-1} was observed. Also present in the spectra was the CF_4 band at 630 cm^{-1}. Spectra of the evacuated cell and of BF_3 alone were taken in the region mentioned above to substantiate the identification. The cell used was 8 cm long and had polyethylene windows, 0.0625 in. thick.

6.0 Calibration Experiments

Fourteen calibration experiments were made in which benzoic acid (Standard Sample 391) was burned in a platinum crucible in the presence of 30 atm of oxygen and one ml. of distilled water in the nickel combustion bomb. Initially ten calibration experiments were made, and when the heat measurements on the various samples had been completed, an additional set of four calibration experiments was performed. The two sets of calibration data were found to be statistically equivalent differing by six parts in 100,000, and in similar agreement with six calibration experiments performed earlier [1]. All twenty experiments were combined to give a single energy equivalent of 14,803.27 ±0.99 J deg^{-1}. The uncertainty cited is the standard deviation of the mean. The energy equivalent given is that for the standard calorimeter, which consisted of 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 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 grams.

Using the appropriate heat capacity data, the energy equivalent of the standard calorimeter to be used in the fluorine combustion experiments was calculated. Subtracting the heat capacities of 30 atm of oxygen, one ml. of water and the platinum ware, and adding values for 21 atm of fluorine and two aluminum electrodes gave 14,805.17 J deg^{-1}.

7.0 Fluorine Combustion Experiments

Seventeen heat measurements were made on the combustion of Teflon in fluorine, ten on boron-Teflon mixtures, eight on boron carbide-Teflon mixtures, seven on graphite-Teflon mixtures, eleven on aluminum diboride-Teflon mixtures, eleven on α-aluminum dodecaboride mixtures and two on γ-aluminum dodecaboride mixtures. As had been stated earlier, part of the aluminum diboride and α-aluminum dodecaboride data are from previous work [1] and have been combined with new data in calculating heats of combustion and formation.

A fluorine pressure of about 21 atm was used in all experiments except two Teflon, nine α-AlB_{12} and five AlB_2 experiments in which about 16 atm was used. In each experiment the sample pellet was placed in the recess of the monel holder or "A" nickel plate, the bomb attached to the fluorine manifold and filled to the desired fluorine pressure. All bomb parts (bomb base, bomb head assembly and electrodes, liner and sample plate) were weighed before the first experiment and after each experiment. The bomb parts were washed with water and dried before the weighings were made.

Tables 5 through 12 give the data for the individual experiments on Teflon, boron, boron carbide, graphite, aluminum diboride, α-aluminum dodecaboride and γ-aluminum dodecaboride, respectively.

Table 5

Teflon 5 Combustion Experiments

Experiment No.	1	2	3	4	5	6	7	8	9	10
(1b) Teflon, g.	4.229495	4.319060	4.286609	4.285883	4.358344	4.354427	4.362010	4.477871	4.367548	4.359840
(2) F_2 press. atm.	21.7	21.8	21.8	16.7	16.6	21.8	21.3	21.4	22.0	22.1
(3) ε, J deg^{-1}	14,809.37	14,809.26	14,808.68	14,806.99	14,802.71	14,805.08	14,804.39	14,801.45	14,801.91	14,801.94
(4) Δt_c, deg.	2.96617	3.02828	3.00590	3.00367	3.05546	3.05400	3.05916	3.14084	3.06293	3.05710
(5) $(\varepsilon)(-\Delta t_c)$, J	-43,927.1	-44,846.6	-44,513.4	-44,475.3	-45,229.1	-45,214.7	-45,289.0	-46.489.0	-45,337.2	-45,251.0
(6) ΔE fuse, J	36.9	37.6	32.3	35.1	14.9	13.7	15.5	15.6	15.8	16.0
(7) ΔE gas, J	19.7	20.3	19.7	16.1	16.1	20.4	20.0	20.7	20.6	20.6
(9) ΔE°_{303}, Jg^{-1}	-10,372.5	-10,370.0	-10,372.2	-10,365.2	-10,370.5	-10,375.8	-10,374.5	-10,373.8	-10,372.1	-10,370.7

(10) $\Delta E^\circ_{303} = -10{,}371.7\ Jg^{-1}$

(11) Std. Dev. Mean 0.93 Jg^{-1}

(13) $\Delta E^\circ_{298} - \Delta E^\circ_{303} = 3.4\ Jg^{-1}$

(14) $\Delta E^\circ_{298} = -10{,}368.3\ Jg^{-1}$

(15) $\Delta nRT = 0$

(16) $\Delta H^\circ_{298} = -10{,}368.3\ Jg^{-1}$

Table 6

Teflon 7 Combustion Experiments

Experiment No.	1	2	3	4	5	6	7
(1b) Teflon, g.	4.446597	4.367727	4.546440	4.443729	4.472263	4.367187	4.395447
(2) F_2 press. atm.	22.1	22.1	22.2	22.3	22.2	21.9	22.0
(3) ε, J deg^{-1}	14,801.56	14,801.93	14,801.94	14,802.21	14,762.58	14,718.29	14,760.24
(4) Δt_c, deg	3.11882	3.06456	3.18913	3.11615	3.14506	3.08065	3.09083
(5) (ε) ($-\Delta t_c$), J	-46,163.4	-45,361.4	-47,205.3	-46,125.9	-46,429.2	-45,341.9	-45,621.4
(6) ΔE fuse, J	18.9	19.4	18.6	17.5	19.9	19.5	20.4
(7) ΔE gas, J	21.1	21.0	21.7	21.3	21.4	20.5	20.8
(9) ΔE^{o}_{303}, J g^{-1}	-10,372.7	-10,376.3	-10,374.1	-10,371.3	-10,372.4	-10,373.2	-10,369.9

(10) $\Delta E^{o}_{303} = -10{,}372.8$ J g^{-1}

(11) Std. Dev. Mean 0.77 J g^{-1}

(13) $\Delta E^{o}_{298} - \Delta E^{o}_{303} = 3.4$ J g^{-1}

(14) $\Delta E^{o}_{298} = -10{,}369.4$ J g^{-1}

(15) $\Delta nRT = 0$

(16) $\Delta H^{o}_{298} = -10{,}369.4$ J g^{-1}

Table 7

Boron-Teflon 7 Combustion Experiments

Experiment No.	1	2	3	4	5	6	7	8	9	10
(1a) boron, g.	0.157445	0.153855	0.151491	0.153548	0.163776	0.149285	0.152272	0.154050	0.160539	0.167921
(1b) Teflon, g.	2.767867	2.813748	2.675986	2.717357	2.880045	3.243633	3.168021	2.933396	3.053495	2.807121
(2) F_2 press. atm.	21.2	21.6	21.4	21.6	21.4	21.8	21.6	21.9	22.0	21.9
(3) (ε), J deg^{-1}	14,798.95	14,796.70	14,805.56	14,803.17	14,804.61	14,803.77	14,804.26	14,799.88	14,805.01	14,803.61
(4) Δt_c, deg	3.05494	3.06023	2.94249	2.98886	3.17645	3.33155	3.29647	3.14578	3.27706	3.15415
(5) $(\varepsilon)\ (-\Delta t_c)$, J	-45,209.9	-45,281.3	-43,565.2	-44,244.6	-47,026.1	-49,319.5	-48,801.8	-46,557.1	-48,516.9	-46,692.8
(6) ΔE fuse, J	20.2	20.5	20.3	20.4	20.4	20.4	20.4	16.9	17.4	18.5
(7) ΔE gas, J	13.2	13.6	12.8	13.1	13.9	15.8	15.4	14.3	15.1	13.9
(8) $(-\Delta E^\circ$ Teflon)(mb), J	28,710.5	29,186.4	27,757.5	28,186.6	29,874.1	33,645.6	32,861.2	30,427.5	31,573.3	29,117.7
(9) ΔE°_{303} boron, J g^{-1}	-104,583	-104,389	-104,129	-104,362	-104,519	-104,751	-104,450	-104,501	-104,717	-104,470

(10) $\Delta E^\circ_{303} = -104{,}487$ J g^{-1}

(11) Std. Dev. Mean = 57 J g^{-1} = 0.15 kcal $mole^{-1}$

(12) impurity corr. = 556 J g^{-1} for 0.869% impurities

(13) $\Delta E^\circ_{298} - \Delta E^\circ_{303} = 4$ J g^{-1}

(14) $\Delta E^\circ_{293} = -104{,}838$ J g^{-1}

(15) $\Delta nRT = -350$ J g^{-1}

(16) $\Delta H^\circ_{298} = -105{,}188$ J g^{-1} = -271.82 kcal $mole^{-1}$

Table 8

Boron Carbide-Teflon 7 Combustion Experiments

Experiment No.	1	2	3	4	5	6	7	8
(1a) boron carbide, g.	0.201948	0.184980	0.178836	0.179005	0.182011	0.172072	0.178745	0.168138
(1b) Teflon, g.	2.775820	2.738097	2.776954	2.709381	3.028289	2.895316	2.806986	3.123387
(2) F_2 press atm.	21.5	21.7	22.1	21.3	21.4	22.3	21.1	21.3
(3) (ε) J deg^{-1}	14,800.14	14,804.85	14,804.13	14,799.56	14,805.42	14,800.13	14,804.42	14,804.25
(4) Δt_c, deg	3.27109	3.13267	3.11938	3.07716	3.31773	3.16025	3.14252	3.29554
(5) $(\varepsilon)(-\Delta t_c)$, J	-48,412.6	-46,378.7	-46,179.7	-45,540.6	-49,120.4	-46,772.1	-46,523.2	-48,788.0
(6) ΔE fuse, J	18.5	17.4	18.6	17.5	20.3	20.4	20.4	18.8
(7) ΔE gas, J	13.1	12.9	13.3	12.5	13.9	14.0	12.9	14.5
(8) $(-\Delta E^\circ$ Teflon)(mb), J	28,793.0	28,401.7	28,804.8	28,103.9	31,411.8	30,032.5	29,116.3	32,398.3
(9) ΔE°_{303} B_4C, J g^{-1}	-96,995.3	-97,019.7	-96,977.1	-97,241.4	-97,106.2	-97,082.6	-97,197.7	-97,279.6

(10) $\Delta E^\circ_{303} = -97{,}112.5$ J g^{-1}

(11) Std. Dev. Mean = 40.8 J g^{-1} = 0.5 kcal $mole^{-1}$

(12) Impurity corr. = 196.4 J g^{-1} for 0.700% impurities

(13) $\Delta E^\circ_{298} - \Delta E^\circ_{303} = 3.6$ J g^{-1}

(14) $\Delta E_{298} = -97{,}595.7$ J g^{-1}

(15) $\Delta nRT = -136.8$ J g^{-1}

(16) $\Delta H^\circ_{298} = -97{,}732.5$ J g^{-1} = -1290.7 kcal $mole^{-1}$ (mole = B_4C)

Table 9

Graphite-Teflon 7 Combustion Experiments

Experiment No.	1	2	3	4	5	6	7
(1a) graphite, g.	0.243088	0.255922	0.264152	0.251913	0.256820	0.256785	0.252724
(1b) Teflon, g.	2.419090	2.475588	2.468792	2.592377	2.478479	2.593593	2.468206
(2) F_2 press. atm.	21.1	21.6	22.1	21.8	21.6	21.4	21.5
(3) ε, J deg^{-1}	14,758.06	14,757.62	14,749.66	14,749.65	14,760.77	14,785.54	14,760.23
(4) Δt_c, deg	2.97695	3.08524	3.12481	3.14697	3.09070	3.16518	3.06065
(5) $(\varepsilon)(-\Delta t_c)$, J	-43,934.0	-45,530.8	-46,089.9	-46,416.7	-45,621.1	-46,789.9	-45,175.9
(6) ΔE fuse, J	17.2	18.9	20.4	19.5	16.0	16.0	20.4
(7) ΔE gas, J	8.4	8.8	9.4	9.4	8.8	9.3	8.7
(8) $(\Delta E^\circ$ Teflon)(mb), J	25,092.7	25,678.8	25,608.3	26,890.2	25,708.8	26,902.8	25,602.2
(9) ΔE°_{303}, graphite, J g^{-1}	-77,402.8	-77,462.3	-77,424.4	-77,398.1	-77,437.5	-77,383.0	-77,335.7

(10) $\Delta E^\circ_{303} = -77{,}406.3$ J g^{-1}

(11) Std. Dev. Mean = 15.5 J g^{-1} = 0.04 kcal $mole^{-1}$

(12) Impurity corr. = 0.0 J g^{-1} for 0.029% impurities

(13) $\Delta E^\circ_{298} - \Delta E^\circ_{303} = 4.2$ J g^{-1}

(14) $\Delta E^\circ_{298} = -77{,}424.6$ J g^{-1}

(15) $\Delta nRT = -209.8$ J g^{-1}

(16) $\Delta H^\circ_{298} = -77{,}634.4$ J g^{-1} = -222.87 kcal $mole^{-1}$

Table 10a

Aluminum Diboride-Teflon 5 Combustion Experiments

Experiment No.	1	2	3	4	5
(1a) $A\ell B_2$, g.	0.346897	0.315264	0.289106	0.302016	0.289516
(1b) Teflon, g.	1.867781	2.002869	1.931063	2.026699	2.035973
(2) F_2 press. atm.	16.7	16.4	16.7	16.8	16.8
(3) (ε), J deg^{-1}	14,805.57	14,805.09	14,805.32	14,804.45	14,803.95
(4) Δt_c, deg	3.03427	2.97751	2.80252	2.92554	2.87476
(5) $(\varepsilon)(-\Delta t_c)$, J	-44,924.1	-44,082.3	-41,492.2	-43,311.0	-42,557.8
(6) ΔE fuse, J	41.6	42.3	41.7	42.3	41.5
(7) ΔE gas, J	4.5	5.2	5.0	5.5	4.7
(8) $(-\Delta E^\circ$ Teflon)(mb), J	19,372.1	20,773.2	20,028.4	21,020.3	21,116.5
(9) $\Delta E^\circ_{303} A\ell B_2$, J g^{-1}	-73,525.9	-73,784.5	-74,080.4	-73,648.1	-73,899.5

(10) ΔE°_{303}, = -73,787.7 J g^{-1}

(11) Std. Dev. Mean = 96.5 J g^{-1} = 1.17 kcal $mole^{-1}$

(12) Impurity corr. = 687.8 J g^{-1} for 2.771% impurities
using Treatment (3), Table 16

(13) $\Delta E^\circ_{298} - \Delta E^\circ_{303} = -2.7$ J g^{-1}

(14) ΔE°_{298} = -75,185.9 J g^{-1}

(15) $\Delta nRT = -139.7$ J g^{-1}

(16) $\Delta H^\circ_{298} = -75,325.6$ J g^{-1} = -916.87 kcal $mole^{-1}$ (mole = $A\ell B_{2.215}$)

Table 10b

Aluminum Diboride-Teflon 5 Combustion Experiments

Experiment No.	6	7	8	9	10	11
(1a) $A\ell B_2$, g.	0.267374	0.253674	0.220437	0.222195	0.226260	0.234477
(1b) Teflon, g.	2.999471	2.846011	2.897229	2.957633	2.875395	2.933704
(2) F_2 press. atm.	21.9	21.8	21.5	21.6	21.5	21.7
(3) (ε), J deg^{-1}	14,805.63	14,805.88	14,803.19	14,803.25	14,803.30	14,801.49
(4) Δt_c, deg	3.48196	3.29846	3.16402	3.21878	3.18094	3.26692
(5) $(\varepsilon)(-\Delta t_c)$, J	-51,552.6	-48,830.0	-46,837.6	-47,648.4	-47,088.4	-48,355.3
(6) ΔE fuse, J	20.4	20.4	20.4	20.4	20.4	20.4
(7) ΔE gas, J	11.8	11.0	11.4	11.5	11.2	11.5
(8) $(-\Delta E^\circ$ Teflon)(mb), J	31,109.6	29,518.0	30,049.2	30,675.7	29,822.7	30,427.5
(9) ΔE°_{303} $A\ell B_2$, J g^{-1}	-76,338.0	-76,005.4	-76,015.4	-76,242.9	-76,169.5	-76,322.6

(10) ΔE°_{303} = -76,182.3 J g^{-1}

(11) Std. Dev. Mean = 59.7 J g^{-1} = 0.73 kcal $mole^{-1}$

(12) Impurity corr. = 731.7 J g^{-1} for 2.768% impurities using Treatment (3), Table 16

(13) $\Delta E^\circ_{298} - \Delta E^\circ_{303}$ = -2.7 J g^{-1}

(14) ΔE°_{298} = -77,601.2 J g^{-1}

(15) ΔnRT = -139.7 J g^{-1}

(16) ΔH°_{298} = -77,740.9 J g^{-1} = -946.27 kcal $mole^{-1}$ (mole = $A\ell B_{2.215}$)

Table 11

α-Aluminum Dodecaboride-Teflon 5 Combustion Experiments

Experiment No.	1	2	3	4	5	6	7	8	9	10	11
(1a) α-$A\ell B_{12}$, g.	0.313053	0.319321	0.306651	0.311374	0.286230	0.305196	0.305665	0.345568	0.318994	0.200065	0.237862
(1b) 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) F_2 press. atm	16.6	16.4	16.7	16.8	16.9	16.9	16.8	16.6	16.8	21.6	21.5
(3) (ε), J deg^{-1}	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) Δt_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) $(\varepsilon)(-\Delta t_c)$, 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) ΔE 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) ΔE 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)(mb), 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) ΔE°_{303} α-$A\ell B_{12}$, J g^{-1}	-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) ΔE°_{303} = -92,926.5 J g^{-1}

(11) Std. Dev. Mean = 45.8 J g^{-1} = 1.7 kcal $mole^{-1}$

(12) Impurity corr. = 1,027.7 J g^{-1} for 3.210% impurities using treatment (4) Table 17.

(13) $\Delta E^\circ_{298} - \Delta E^\circ_{303} = -0.5$ J g^{-1}

(14) ΔE°_{298} = -94,944.4 J g^{-1}

(15) ΔnRT = -120.6 J g^{-1}

(16, ΔH°_{298} = -95,065.0 J g^{-1} = -3560.7 kcal $mole^{-1}$

Table 12

γ-Aluminum Dodecaboride-Teflon 5 Combustion Experiments

Experiment	1	2
(1a) γ-AlB_{12}, g.	0.214193	0.199240
(1b) Teflon, g.	2.881544	2.698701
(2) F_2 press. atm.	21.5	22.0
(3) (ε), J deg^{-1}	14,799.18	14,804.01
(4) Δt_c, deg	3.40060	3.17741
(5) (ε)($-\Delta t_c$), J	-50,326.1	-47,038.4
(6) ΔE fuse, J	20.4	20.4
(7) ΔE gas, J	13.3	12.6
(8) ($-\Delta E^\circ$ Teflon)(mb), J	29,886.5	27,990.1
(9) ΔE°_{303} γ-AlB_{12}, J g^{-1}	-95,268.8	-95,439.2

(10) ΔE°_{303} = -95,354.0 J g^{-1}

(11) Std. Dev. Mean
= 9.2 J g^{-1} = 0.34 kcal $mole^{-1}$

(12) Impurity corr. = 4365.2 J g^{-1} for 4.766% impurities
using treatment (4) Table 18

(13) $\Delta E^\circ_{298} - \Delta E^\circ_{303}$ = -0.5 J g^{-1}

(14) ΔE°_{298} = -95,542.8 J g^{-1}

(15) ΔnRT = -120.6 J g^{-1}

(16) ΔH°_{298} = -95,663.4 J g^{-1} = -3583.1 kcal $mole^{-1}$

The numbered entries in the Tables are as follows:

(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 (2):

$$W(c) + 3F_2(g) = WF_6(g) \qquad (2)$$

From the heat of formation of WF_6 [59], we calculate 9.44 J mg^{-1} for the energy of combustion of the fuse.

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

$$\Delta E\ \text{gas} = \Delta E^{i}(\text{gas})\Big]_{0}^{P_i(\text{gas})} + \Delta E^{f}(\text{gas})\Big]_{P_f(\text{gas})}^{0}$$

(8) standard energy of combustion per gram of Teflon at 30°C multiplied by the corrected mass of Teflon in the pellet, (mb).

(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) correction for impurities.

(13) heat capacity correction converting the reference temperature to 298°K.

(14) standard energy of combustion corrected for impurities at 298°K.

(15) ΔnRT correction

(16) standard enthalpy of combustion at 298°K.

The heat capacities at constant pressure, C_p, used in the calculation of entry (13) are as follows in cal deg^{-1} gram^{-1} at 25°C: aluminum, 0.216 [60]; boron, 0.245 [34]; Teflon, 0.28 [17], boron carbide, 0.228 [34]; graphite, 0.170 [60]; aluminum diboride, 0.0907; α-aluminum dodecaboride, 0.0853; γ-aluminum dodecaboride, 0.0853; aluminum fluoride, 0.213 [60]; fluorine, 0.197 [60]; carbon tetrafluoride, 0.166 [61]; boron trifluoride 0.178 [34]; and calcium fluoride, 0.205 [29]. The heat capacities of AlB_2, α-AlB_{12}

and γ-$A\ell B_{12}$ 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 used in the calculation of entry (3) for fluorine, carbon tetrafluoride and boron trifluoride at 30°C were 5.52 [60], 12.62 [61], and 10.04 [34] cal deg^{-1} mole^{-1}, respectively.

Washburn corrections in entry (7) were calculated following the procedure outlined by Hubbard [62] 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 [63] using the appropriate force constants. The force constants used for fluorine, carbon tetrafluoride and boron trifluoride were those determined by White, Hu and Johnston [64], Douslin [65], and Brooks and Raw [66], respectively. Force constants appropriate to the mixtures of F_2 and CF_4, and F_2, CF_4 and BF_3 in the reaction products were calculated from those for the pure components.

In calculating the corrections for the combustion of impurities in the samples, and in calculating the heats of formation of the aluminum borides, the following values, in kcal mole^{-1}, were used for the heats of formation of other compounds: $A\ell F_3$, -360.4 [2]; $A\ell_2O_3$, -400.4 [67]; B_2O_3, -305.34 [68]; $A\ell_4C_3$, -49.7 [6]; $A\ell N$, -76.0 [60]; BN, -59.51 [69]; MgF_2, -268.7 [70]; CaF_2, -290.3 [29]; SiF_4, -385.98 [76]; FeF_3, -235 [72]; CuF_2, -126.9 [29]; MnF_3, -238 [72]; SrF_2, -290.3 [29]; TiF_4, -394.19 [73]; and ZrF_4, -456.80 [74].

Atomic weights were taken from the 1961 table of atomic weights based on carbon-12 and adopted by the Internationa Union of Pure and Applied Chemistry [75]. The unit of energy is the Joule, and calorie was taken as 4.1840 J.

The raw data obtained in the benzoic acid calibration experiments was programmed for the 7094 computer according to procedures outlined by C. Howard Shomate for the computer calculation of combustion bomb calorimetric data. The combustion experiments were similarly programmed, however, the only valid data calculated by the computerwas the corrected temperature rise, Δt_c, because the program used had not been modified to accommodate the use of fluorine as the oxidant.

About 500 mg of crystalline boron was transformed into a boric acid solution by pyrohydrolysis [79] and the solution examined by surface emission mass spectrometry for the isotopic abundance of B^{10}/B^{11}. This study resulted in the atomic weight determination of our sample of 10.812 ±0.005. The uncertainty cited is a best estimate and is not absolute.

8.0 Discussion and Results

8.1 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.

Twelve Teflon combustion experiments were performed in which the residue remaining after the combustion of a pellet was accurately weighed, collected with alundum powder, and analyzed for carbon. The technique consisted of determining the carbon gravimetrically after combustion in the Coleman carbon-hydrogen analyzer. The average mass of the residue was about 0.90 mg (range 0.46 to 1.22 mg) while carbon content was found to be on the average 0.09 mg (range 0.05 to 0.15 mg). Three blank experiments were performed in which a weighed amount of graphite powder mixed with alundum powder was submitted for analysis along with the Teflon residues. The graphite samples weighed 7.99 mg, 1.70 mg and 0.92 mg; the carbon found was 7.12 mg, 0.80 mg and 0.34 mg, respectively. These results implied that the analytical method was valid for graphite samples of about 5 mg, but was systematically low for samples of a few mg.

Two experiments were performed (Table 5b experiment 9, Table 6 experiment 7) in which a 0.3 gram Teflon bag was filled with Teflon powder, pressed and burned in fluorine in order to determine whether the presence of the Teflon bag affects the heat of combustion of Teflon. Another similar experiment was performed (Table 5 experiment 10) in which a Teflon bag filled with Teflon powder was pressed and coated with an outer layer of Teflon. Combustion of neither this Teflon pellet nor the two uncoated Teflon pellets showed any departure from the expected value for the heat of combustion in fluorine. Examination of combustion residues showed about the same mass of carbon present here as for residues with no bag.

When a pelleted mixture is burned in fluorine, it is exceedingly difficult to obtain both an analysis for the unreacted principal constituent, such as boron or an aluminum boride, and also carbon. However, several non-calorimetric experiments were performed in which pellets of boron-Teflon, B_4C-Teflon, $A\ell B_2$-Teflon, α-$A\ell B_{12}$-Teflon and γ-$A\ell B_{12}$-Teflon were burned in fluorine and the residues analyzed for carbon. The results are shown in Table 13.

Table 13

Carbon Analysis on Residues of Pelleted Mixtures

Pellet	Method of Preparing Pellet	Initial F_2 Pressure, atm.	Mass Carbon in Residue, mg
boron-Teflon	III	21	0.12
B_4C-Teflon	III	21	0.08
AlB_2-Teflon	III	21	0.33
α-AlB_{12}-Teflon	I	16	0.17
γ-AlB_{12}-Teflon	II	21	0.49, 0.59

Inspection of Table 13 shows that the carbon content of combustion residues formed by burning boron-Teflon or B_4C-Teflon pellets in fluorine is comparable to those found when Teflon is burned alone. The carbon found in the AlF_3 residue formed from burning an α-AlB_{12}-Teflon pellet in 16 atm of fluorine in which no Teflon bag was employed, was similarly small. However, in the case of AlB_2-Teflon and γ-AlB_{12}-Teflon pellets in which the Teflon bag or Teflon bag and coating was used, a residue three to six times the average found in a carbon analysis of a Teflon residue was observed. We suspect that when one of the combustion products is non-volatile, such as aluminum fluoride, and a Teflon bag is used in preparing a pellet, quenching of the final remaining amounts of the burning pellet is more easily accomplished. It will be mentioned shortly in the discussion of the boron analysis of AlF_3 residues from the combustion of AlB_2-Teflon and α-AlB_{12}-Teflon residues, that the boron recovered, i.e., aluminum boride, is much less when Method I is used to prepare the sample than when Methods II or III, which requires a Teflon bag, is employed.

Five samples of alundum powder were submitted for blank carbon analyses and an average of 0.04 mg (range 0.01 to 0.07 mg) was calculated, slightly reducing each carbon determination performed.

After a boron-Teflon combustion experiment, a residue was found weighing approximately three mg, of which 0.5 to 1.1 mg was found to be boron. The residue was taken up from an "A" nickel plate by mixing and rubbing Na_2CO_3 into the residue with a spatula. Analysis of the Na_2CO_3-residue mixture was made by the NBS Analysis and Purification Section where it was fused with K_2CO_3 and put into solution with 5N HCl. The pH of the solution was adjusted, mannitol added, and the boric acid formed titrated with base.

After a boron carbide-Teflon combustion experiment, a residue was found weighing about one mg of which 0.13 mg to 0.19 mg was found to be unburned boron carbide. The manner in which the residue was gathered from the "A" nickel plate and analyzed for boron (and consequently boron carbide) was the same as with the boron-Teflon combustion residues.

Aluminum fluoride residues obtained from the combustion of $A\ell B_2$-Teflon and α-$A\ell B_{12}$-Teflon mixtures prepared by means of Method I were analyzed for boron content in order to determine the amount of unreacted aluminum boride. The $A\ell F_3$ 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 [76]. The recovery of unburned $A\ell B_2$ ranged from 0.10 to 0.24 mg while that for α-$A\ell B_{12}$ was between 0.01 and 0.04 mg.

Aluminum fluoride residues obtained from the combustion of $A\ell B_2$-Teflon, α-$A\ell B_{12}$-Teflon and γ-$A\ell B_{12}$-Teflon mixtures using Methods II or III as the preparation technique were treated similar to those whose samples were prepared by Method I except for a few differences. After the fusion, the sample was put into solution with 5N H_2SO_4 and the boron determined spectrophotometrically using methylene blue. The recovery ranged between 0.07 to 0.16 mg for $A\ell B_2$, and 0.34 to 0.41 mg for α-$A\ell B_{12}$ and γ-$A\ell B_{12}$, respectively.

The masses of residues obtained as a result of burning a graphite-Teflon pellet varied depending upon the type of support used and particle size of the graphite. These variations are shown in Table 14 along with a carbon analysis of the residue.

Table 14

Completeness of Graphite-Teflon Combustion Experiments

Exper. No.	Particle Size of Graphite, range in microns	Type of Sample Support Used	Mass Combustion Residue mg	Mass Carbon in Residue mg
1	150 - 420	45 g. nickel plate	10.31	5.17
2	150 - 420	44 g. nickel plate	13.22	7.11
3	150 - 420	25 g. nickel plate	7.78	4.17
4	150 - 420	25 g. nickel plate	10.18	5.88
5	150 - 420	25 g. nickel plate and 13 g CaF_2 plate	3.02	1.93
6	40 - 150	26 g. nickel plate and 13 g CaF_2 plate	1.74	0.83
7	40 - 150	25 g. nickel plate and 13 g CaF_2 plate	0.80	0.28

By reducing the thickness of the "A" nickel plate from 0.125 in. (45 g.) to 0.0625 in. (25 g.), no significant improvement in the degree of completeness of reaction was noted. However, improvement came with use of the 0.0625 in. thick nickel plate and a 0.125 in. thick CaF_2 plate underneath, increasing the completeness of combustion from about 97 percent to better than 99 percent. Further improvement in the degree of completeness came by grinding the sample to a smaller particle size (40-150 microns), and brought reactions to 99.7 to 99.9 percent completion. The percent completion was calculated using the mass of carbon found in the residue as compared to the initial mass of graphite in the sample. However, the large difference in mass between the weighed residue and the carbon determined by analyses cannot be ignored. In order to resolve this disparity two non-calorimetric combustion experiments were performed in which graphite-Teflon pellets were burned in 21 atm of fluorine and residues analyzed for fluorine content. The residues weighed 13.77 mg and 4.20 mg and were found to contain 4.8 mg and 1.1 mg of fluorine, respectively. Another non-calorimetric combustion of Teflon alone in 21 atm of fluorine gave a residue of 0.65 mg and contained 0.16 mg of fluorine. Another Teflon residue weighing 0.51 mg was similarly prepared and analyzed for nickel content, showing 0.03 mg of nickel present.

Besides fluorine and nickel being likely constituents of the remainder of the residue, another factor may be playing a significant role, namely the tungsten fuse. We observed that tiny balls assumed to be melted tungsten were sprayed atop of the "A" nickel plate as a result of fuse ignition ranging in diameter from 0.004 in. to 0.014 in. If we assume ten balls of molten tungsten are sprayed on the "A" nickel plate per experiment having an average diameter of 0.008 in., a mass increment of 0.08 mg should be observed. We believe if one considers the carbon, fluorine and nickel analyses errors, and the tungsten mass increment assumption, a reasonable, although quantitatively incomplete, solution to the mass disparity can be found.

8.2 Relation of the Method of Sample Preparation to Premature Combustion

Attempts to burn pellets of boron mixed with Teflon in 21 atm of fluorine using Methods I or II to prepare the sample resulted in spontaneous combustion of the pellet during the fluorine loading procedure. However, no spontaneous combustion occurred when Method III, using a Teflon coated pellet, was employed to prepare the sample. Cooling constants calculated for the combustion reactions were comparable to a normal combustion experiment in which no premature reaction was taking place.

As a precautionary measure, B_4C-Teflon pellets were prepared using Method III in order to maintain maximum protection of the sample from spontaneous combustion or premature reaction prior to the desired time of ignition.

Combustions of graphite-Teflon pellets were made using Methods II and III, and from the data no significant effects appear to have taken place due to the presence or absence of a Teflon coating around the pellet.

In the case of α-$A\ell B_{12}$-Teflon combustions, preparation of the sample using Method I appeared suitable. This fact was tested by also performing heat measurements on α-$A\ell B_{12}$-Teflon mixtures prepared by Methods II and III. If the pellets prepared using Method I were undergoing reaction prior to ignition of the sample, heat measurements made using pellets prepared by Methods II and III should give more negative heats of combustion. This was not the case. As a matter of fact the latter two experiments, (nos. 10 and 11, Table 11), gave low values for the heat of combustion which might be attributed to the use of a Teflon bag as mentioned in Section 8.1 and illustrated in Table 13.

Two heat measurements were performed in which γ-$A\ell B_{12}$-Teflon pellets were burned in 21 atm of fluorine using Method II to prepare the samples. The calculated heat of combustion for γ-$A\ell B_{12}$ was found to be more negative than for α-$A\ell B_{12}$. An analysis of this situation is given in Section 9.0 on the heat of formation of γ-$A\ell B_{12}$.

A slow reaction was detected prior to ignition of the $A\ell B_2$-Teflon pellets when Method I was used. The rate of temperature rise during the fore-period when the calorimeter is about three degrees below the jacket temperature was observed to be 4×10^{-5} to 5×10^{-5} ohms $\min^{-1}$ higher than normal and led to unusually high values for the calorimeter cooling constant.

At the time this work was done [1], an estimate of the fore-period reaction was attempted by correlating the heat of combustion of each $A\ell B_2$-Teflon experiment with its abnormally high cooling constant. A recalculation of the data has revealed an error in one of the experiments disrupting the trend which implied that a high cooling constant gave a low heat of combustion for a given experiment. In view of this feature of the latter $A\ell B_2$ experiments and because another series of heat measurements on $A\ell B_2$-Teflon mixtures has been performed in which the premature reaction of $A\ell B_2$ prior to ignition appears absent, no further treatment of this data will be made.

Six heat measurements were made in which AlB_2-Teflon pellets were burned in 21 atm of fluorine using Method III as the technique to prepare samples for combustion. The cooling constants observed for these experiments were normal. The observed heat of combustion given in Table 10b is 29.85 kcal $mole^{-1}$ more negative than that calculated in Table 10a for aluminum diboride, in which Method I was used for sample preparation. The heat of combustion of aluminum diboride given in Table 10b, -947.12 kcal $mole^{-1}$, is preferred over that given in Table 10a since it requires no gross correction for premature reaction.

8.3 Mass Increments of Pellets Exposed to Fluorine

Pellets of Teflon were exposed to fluorine in the combustion bomb as seen in the first three tests of Table 15. After prolonged exposure to fluorine, Teflon pellets have not returned to their original mass even after treatment in vacuum as shown in tests 1 and 2. Reaction of the fluorine absorbed in the pellet with moist air could have resulted in the formation of some hydrofluoric acid. Test 3 implied that short exposure to fluorine by a Teflon pellet involved a small mass increment of about 0.06 mg and a return to the original mass was possible in a relatively short time interval. If the interaction of Teflon and fluorine results in reaction to carbon tetrafluoride, an ultimate decrease in mass should have been observed. Test 4 showed that as much as 0.4 mg can be lost as a consequence of being under vacuum. This implies that a Teflon pellet formed from powder by compression may be porous in nature. Under high pressure a Teflon pellet may absorb a gas and after being returned to atmospheric pressure will slowly release the gas. The degree of absorption or retention would be difficult to estimate because of slow-equilibration to the original gas content of the pellet.

In the case of pelleted mixtures, we feel that interpretation of the mass increments observed as a result of exposure to fluorine is complicated by moist air enhancing reaction between the fluorine that has been absorbed in the Teflon and the sample mixed with the Teflon. Estimating whether reaction between fluorine and the sample is taking place in the bomb and/or being propagated as a result of exposure of the pellet to moist air is very difficult to determine.

In tests 5 and 6, in which boron-Teflon and B_4C-Teflon pellets were exposed to fluorine, mass increments appear to be affected by moisture and a decrease in mass is observed as a result of treatment under vaccum or exposure to a dry atmosphere.

In the case of exposure to fluorine of a graphite-Teflon pellet, although a large mass increment was initially observed, 5.5 mg, a continued decrease in mass implied a lesser affect from exposure to moist air and possibly a physical rather than chemical process taking place.

In test 8, reaction of fluorine with $A\ell B_2$ is observed and is further substantiated by an unusually high initial drift rate of the calorimeter in the fore period of the experiment. Also apparent is the effect of moist air upon the observed mass increment. In test 9, the coated Teflon pellet technique was used and a substantial decrease in apparent reaction is observed. The effects of moist air upon the pellet are present but it is difficult at this point to decide what fraction of the initial mass increment was obtained from reaction with fluorine in the bomb or by the interaction of moisture from the air after removal of the pellet. If reaction was taking place in the bomb, it was small enough so it did not effect the initial drift of the calorimeter since normal cooling constants were obtained.

Tests 10 and 11 show the gain in mass of an α-$A\ell B_{12}$-Teflon pellet after exposure to fluorine. The results of test 11 show the effect of moisture upon the pelleted mixture and imply the interaction of moisture with the pellet is very pronounced in the first few minutes of exposure to the air.

With the exception of test no. 8, we feel that the data in Table 15, although indicative of reaction, is not necessarily indicative of events taking place in the combustion bomb prior to ignition of the sample. However, since our data does not permit unequivocal interpretation of the mass increments, we have allowed for the possibility of reaction of the sample prior to ignition in our estimate of the accuracy of the heat measurements in Section 8.5.

Table 15

Mass Increments of Pellets After Exposure to Fluorine

Test No.	Type of Pellet and Method of Preparation	Initial Mass of Pellet, m_o grams	Estimated Time Interval from Removal of Pellet from Bomb to Weighing	Conditions (1) and Mass Change $m_1 - m_0$, mg	Conditions (2) and Mass Change $m_2 - m_0$, mg	Conditions (3) and Mass Change $m_3 - m_0$, mg	Conditions (4) and Mass Change $m_4 - m_0$, mg
1	Teflon 7	4.24234	30 min.	in bomb, 21 atm F_2 21 hours +0.61	exposed to air 1.5 days +0.42	exposed to air 15 days and under vac. 7 hours +0.19	exposed to air 12 days +0.24
2	Teflon 5	4.47363	15 min.	in bomb, 16 atm F_2 11 days +2.65	under vacuum 1 day +1.92	exposed to air 6 days +1.05	exposed to air 22 days +0.80
3	Teflon 5	4.23627	30 min.	under vacuum 1.5 hours -0.06	in bomb, 21 atm F_2 6 hours +0.003	under vacuum 30 min. -0.05	
4	Teflon 5	4.36031	15 min.	under vacuum 7 days -0.44			
5	boron-Teflon 7 Method III	2.14969 (198 mg boron)	30 min.	in bomb, 21 atm F_2 3.5 hours +0.88	exposed to air overnight, 16 hrs. +1.11	under vacuum 6 hours +0.70	exposed to air 19 days +1.38
6	B_4C-Teflon 7 Method III	3.26617 (202 mg B_4C)	30 min.	in bomb, 21 atm F_2 5 hours +0.85	in desiccator 5 months +0.43		
7	graphite-Teflon Method II	2.84575 (255 mg, graphite)	15 min.	in bomb, 21 atm F_2 2.3 hours +5.48	exposed to air 3 weeks +4.07	exposed to air 3 weeks +3.50	exposed to air 5 days and vacuum 18 hours +3.34
8	$A\ell B_2$-Teflon 5 Method I	2.21238 (356 mg, $A\ell B_2$)	30 min.	in bomb, 16 atm F_2 5 hours +14.73	exposed to air 1 day +35.13	under vacuum 2 hours +32.40	
9	$A\ell B_2$-Teflon 5 Method III	3.59082 (229 mg, $A\ell B_2$)	15 min.	in bomb, 21 atm F_2 2.3 hours +3.93	exposed to air 3 weeks +15.02	exposed to air 3 weeks +18.98	exposed to air 5 days and vacuum 18 hours +17.52
10	α-$A\ell B_{12}$-Teflon 5 Method I	2.15430 (290 mg, α-$A\ell B_{12}$)	2 hours	in bomb, 16 atm F_2 5 days +3.70			
11	α-$A\ell B_{12}$-Teflon 5 Method I	2.10101 (304 mg, α-$A\ell B_{12}$)	5 min.	in bomb, 16 atm F_2 2.3 hours +1	exposed to air 25 min. +2	exposed to air 1 day +3.70	exposed to air 4 weeks -0.13

8.4 Treatment of Impurities

In all samples, metallic impurities were assumed to be present as the elements. In the boron sample, the oxygen, nitrogen and carbon impurities were assumed present as B_2O_3, BN and B_4C, respectively. The oxygen and nitrogen impurities in the graphite sample were assumed present as the element and to undergo no reaction with the sample.

Difficulty was encountered in calculating heats of combustion and heats of formation for boron carbide and the aluminum borides because of the non-stoichiometric ratios of boron to carbon and boron to aluminum found as a result of chemical analysis. Another problem arises in that the total compositions of boron carbide and γ-AlB_{12} come to much less than 100 percent, namely 98.14 and 97.29 percent. On the other hand AlB_2 and α-AlB_{12} come out 101.59 and 100.41 percent, respectively. In computing the energy contribution of the impurities to the total energy observed, the total composition is normalized to 100 percent and a third problem presents itself. The proportions by which non-metallic elements are combined with the aluminum and boron present in the aluminum borides is unknown, in addition to the nature of the combination involved, i.e., Al_4C_3, B_4C, Al_2O_3, B_2O_3, AlN or BN. In the case of boron carbide, the decision as to the nature of combination of oxygen and nitrogen has been B_2O_3 and BN since the combination of oxygen and nitrogen with carbon results in volatile products.

In considering the possible distribution of the non-metallic impurities in compounds of aluminum and boron, we have chosen three treatments which are designed to show the variations between the probable and unlikely situations. First the compound of aluminum and boron can be considered stoichiometric and the non-metals can be assumed to be combined entirely with one element. Any excess of aluminum or boron remaining is assumed to be present as the free element. This situation gives two extreme possibilities depending upon which element is presumed to be combined with the non-metals. AlB_2, α-AlB_{12} and γ-AlB_{12} have been treated in this manner and the two extreme analyses are shown in columns (1) and (2) of Tables 16, 17 and 18. In treatment (1) the non-metals are combined entirely with aluminum and in treatment (2) they are combined entirely with boron.

Secondly, the compound of aluminum and boron can be considered to be non-stoichiometric and the non-metallic impurities distributed between boron and aluminum in proportion to the relative number of moles of boron and aluminum. In this situation the measured atomic ratios lead to non-stoichiometric compounds having formulas $AlB_{2.215}$, α-$AlB_{11.96}$ and γ-$AlB_{12.57}$. These formulas were adopted for calculation of the results on the basis of the chemical analysis found for boron and aluminum in the respective aluminum boride.

Table 16

Composition of Aluminum Diboride (% by Weight)

Constituent	(1)	(2)	(3)	(4)
$A\ell B_2$	90.532	93.976	-	92.772
$A\ell B_{2.215}$	-	-	97.232	-
$A\ell$	-	-	-	-
B	6.027	3.541	-	4.438
$A\ell_2O_3$	2.091	-	0.651	0.697
B_2O_3	-	1.427	0.983	0.952
$A\ell N$	0.865	-	0.269	0.288
BN	-	0.524	0.360	0.348
$A\ell_4C_3$	0.315	-	0.181	0.189
B_4C	-	0.362	0.154	0.145
Fe	0.025	0.025	0.025	0.025
Cu	0.075	0.075	0.075	0.075
Si	0.026	0.026	0.026	0.026
Mg	0.024	0.024	0.024	0.024
Ca	0.013	0.013	0.013	0.013
Mn	0.01	0.01	0.01	0.01
Total	100.003	100.003	100.003	100.003

Table 17

Composition of α-Aluminum Dodecaboride (% by weight)

Constituent	(1)	(2)	(3)	(4)
α-AlB_{12}	85.028	96.619	-	96.790
α-$AlB_{11.96}$	-	-	96.847	-
Al	-	0.306	-	0.056
B	10.780	-	-	-
Al_2O_3	2.751	-	0.212	0.211
B_2O_3	-	1.878	1.733	1.734
AlN	0.787	-	0.061	0.061
BN	-	0.476	0.439	0.440
Al_4C_3	0.437	-	0.088	0.088
B_4C	-	0.504	0.403	0.403
Mg	0.149	0.149	0.149	0.149
Si	0.050	0.050	0.050	0.050
Ca	0.018	0.018	0.018	0.018
Total	100.000	100.000	100.000	100.000

Table 18

Composition of γ-Aluminum Dodecaboride (% by weight)

Constituent	(1)	(2)	(3)	(4)
$\gamma\text{-}\mathrm{A\ell B}_{12}$	91.795	95.699	-	95.234
$\gamma\text{-}\mathrm{A\ell B}_{12.57}$	-	-	98.981	-
$\mathrm{A\ell}$	-	-	-	-
B	6.968	3.294	-	3.746
$\mathrm{A\ell_2O_3}$	0.786	-	0.058	0.061
$\mathrm{B_2O_3}$	-	0.537	0.497	0.495
$\mathrm{A\ell N}$	0.061	-	0.004	0.005
BN	-	0.036	0.034	0.034
$\mathrm{A\ell_4C_3}$	0.288	-	0.056	0.058
$\mathrm{B_4C}$	-	0.331	0.267	0.265
Mg	0.090	0.090	0.090	0.090
Ca	0.007	0.007	0.007	0.007
Fe	0.005	0.005	0.005	0.005
Total	100.000	100.000	99.999	100.000

The final treatment consists of assuming the aluminum boride to be stoichiometric with the non-metallic impurities being distributed between boron and aluminum in proportion to the stoichiometric number of moles of boron and aluminum. An excess of either boron or aluminum is present to adjust the total composition to its original value.

The manner in which the treatment of impurities in the aluminum borides has effected the respective heats of formation is discussed in Section 9.0 and illustrated in Table 24.

8.5 Summary of Errors

We have attempted to estimate the over-all experimental error for the heats of combustion of the samples studied in this investigation and have summarized the results in Table 19.

As a guide toward estimating the error due to the loss of sample during the pelleting operation, we have used the values found in Table 4, column 9. The total loss of the pellet was not used (Table 4, column 10) since part of the loss was due to sealing the Teflon bag. The estimate of the error in analyzing the main constituents in B_4C and γ-AlB_{12} is somewhat high because of the poor mass balance found from examination of the total compositions obtained for these samples (see Sections 2.2 and 2.5). Similarly, the estimate we chose for the error in analyzing the impurities for the aluminum borides is high because no information was available concerning the distribution of non-metallic impurities in the samples. The carbon analysis for the boron samples as analyzed by two independent laboratories was 0.05 percent and 0.11 percent, respectively, leading to a high impurity error estimate. The data found in Table 13 on the carbon analysis of residues for various pelleted mixtures was used to estimate the error introduced in assuming the Teflon in the pelleted mixture left a residue upon combustion proportional to the mass of Teflon in the pellet.

Errors dealing with weighing of the pellet, analysis of combustion residues, fuse energy and bomb corrosion were usually difficult to estimate on an individual basis and have been introduced as "across the board" corrections. An error for the possible reaction of the sample in the bomb prior to ignition has been introduced since our data on the mass increments of pellets after exposure to fluorine does not definitely preclude its occurrence. Estimates for errors incurred from the benzoic acid calibration experiments, Teflon combustion experiments, and combustion of the sample-Teflon mixtures were made by multiplying the appropriate factor of the t distribution at the 95 percent confidence level by the percent uncertainty in the scatter of the heat measurements. This latter uncertainty was found by dividing the calculated standard deviation of the mean for a particular set of measurement by its average value.

Table 19

Summary of Errors

Description of errors	Error expressed in percent of heat of combustion of sample					
	boron	graphite	B_4C	$AlB_{2.215}$	α-AlB_{12}	γ-AlB_{12}
1. error due to loss during sample preparation (see Table 4, Col. 9)	0.02	0.01	0.02	0.01	0.02	0.01
2. error in weighing pellet	0.01	0.01	0.01	0.01	0.01	0.01
3. error in analysis of main constituents	-	-	0.33	0.14	0.22	0.33
4. error in analysis of impurities	0.09	0.01	0.05	0.10	0.10	0.10
5. error from reaction prior to ignition	0.02	0.02	0.02	0.04	0.04	0.04
6. error in assuming Teflon in mixture burned completely (see Table 13)	0.01	0.02	0.01	0.03	0.02	0.04
7. error in analysis of combustion residue	0.02	0.02	0.02	0.02	0.02	0.02
8. error in fuse energy	0.02	0.02	0.02	0.02	0.02	0.02
9. error from bomb corrosion	0.01	0.01	0.01	0.01	0.01	0.01
10. error in calibration experiments	0.01	0.01	0.01	0.01	0.01	0.01
11. error in energy of combustion of Teflon	0.02	0.02	0.02	0.02	0.02	0.02
12. error in combustion experiments	0.10	0.04	0.09	0.17	0.12	0.09
13. Total error (percent)	0.14	0.06	0.35	0.25	0.30	0.36
14. Total error (kcal $mole^{-1}$)	0.38	0.13	4.5	2.4	10.7	12.9

The total percent error for a given sample was found by taking the square root of the sum of the squares of the individual errors cited. The last entry gives the same total error expressed in kcal mole^{-1} for the respective heat of combustion.

9.0 Heat of Formation Data

The heats of combustion of boron in fluorine and graphite in fluorine are equal to the heats of formation of boron trifluoride and carbon tetrafluoride since reactions (3) and (4) involve the direct combination of the elements.

$$B(c)\ (\beta\text{-rhombohedral phase}) + \frac{3}{2} F_2(g) = BF_3(g) \qquad (3)$$

$$C\ (\text{graphite}) + 2F_2(g) = CF_4(g) \qquad (4)$$

We find ΔH^{o}_{f298} [$BF_3(g)$] = -271.82 ±0.15 kcal mole^{-1} and ΔH^{o}_{f298} [$CF_4(g)$] = -222.87 ±0.04 kcal mole^{-1}, respectively. The uncertainties cited are the standard deviations of the means. The calculated standard heats of formation for boron trifluoride and carbon tetrafluoride are estimated to be accurate within 0.38 kcal mole^{-1} and 0.13 kcal mole^{-1}, respectively. Our value for the heat of formation of $BF_3(g)$ is in good agreement with Johnson's recent work [15] while the data for $CF_4(g)$ appears to be closest to our calculation [2] based upon the heat of combustion of Teflon in fluorine and a reassessment of the heat of formation of Teflon.

Using the heats of formation we found for $CF_4(g)$ and $BF_3(g)$, the heat of formation of boron carbide has been calculated according to reactions (5) and (6).

$$B_{4.40}C(c) + 8.6F_2(g) = CF_4(g) + 4.4\ BF_3(g) \qquad (5)$$

$$B_4C(c) + 8F_2(g) = CF_4(g) + 4BF_3(g) \qquad (6)$$

We calculate ΔH^{o}_{f298} [$B_{4.40}C(c)$] = -27.2 kcal mole^{-1} assuming the sample to be non-stoichiometric and ΔH^{o}_{f298} [$B_4C(c)$] = -19.5 kcal mole^{-1} if a stoichiometric sample is assumed. We estimate the heat of formation to have an over-all experimental error of 5.0 kcal mole^{-1} using the non-stoichiometric treatment and a value of 4.6 kcal mole^{-1} if the stoichiometric approach is used.

The calculation of the heat of formation of boron carbide is summarized in Table 20.

Table 20

Heat of Formation of Boron Carbide

Type of Data	Heat Data kcal mole^{-1}	Over-all Experimental Error, kcal mole^{-1}
$\Delta H^{\circ}_{c298}[B_{4.40}C(c)]$	-1391.7	4.9
$\Delta H^{\circ}_{c298}[B_{4}C(c)]$	-1290.7	4.5
$\Sigma\Delta H^{\circ}_{f298}$ for products (non-stoichiometric)	-1418.9	0.81
$\Sigma\Delta H^{\circ}_{f298}$ for products (stoichiometric)	-1310.2	0.77
$\Delta H^{\circ}_{f298}[B_{4.40}C(c)]$	-27.2	5.0
$\Delta H^{\circ}_{f298}[B_{4}C(c)]$	-19.5	4.6

In view of the problems encountered in obtaining reliable values for the boron and carbon contents of the boron carbide sample we feel that the stoichiometric treatment of the data is to be preferred over the non-stoichiometric method.

We estimate the error in the boron analysis for boron carbide at ±0.2 percent and carbon analysis at ±0.1 percent. If we assume that the stoichiometry of our sample is $B_{4.00}C$, but actually has a boron content high by 0.2 percent and a carbon content low by 0.1 percent yielding a stoichiometry of $B_{4.028}C$, a heat of combustion 7 kcal mole^{-1} more negative will be found. Similarly the heat of formation of boron carbide could have a maximum error of better than 7 kcal mole^{-1} as a result of such an analytical error.

The heat of combustion of aluminum diboride was calculated according to reaction (7).

$$A\ell B_{2.215}(c) + \frac{9.645}{2} F_2(g) = A\ell F_3(c) + 2.215\ BF_3(g) \qquad (7)$$

Using our data for the heat of formation of aluminum fluoride [2] and the heat of combustion data on $A\ell B_{2.215}$ in Table 10b, we calculate for ΔH°_{f298} [$A\ell B_{2.215}(c)$], -16.2 kcal mole^{-1}. Combining the errors for ΔH°_{c298} [$A\ell B_{2.215}(c)$] and ΔH°_{f298} for the products, we estimate the error in the heat of formation of $A\ell B_{2.215}$ to be 2.9 kcal mole^{-1}. The data used to calculate the heat of formation of $A\ell B_{2.215}$ and the corresponding over-all experimental error is shown in Table 21.

Table 21

Heat of Formation of Aluminum Diboride

Type of Data	Heat Data kcal mole^{-1}	Over-all Experimental Error, kcal mole^{-1}
$\Delta H^{\circ}_{c298}[A\ell B_{2.215}(c)]$	-946.27	2.4
$\Sigma\Delta H^{\circ}_{f298}$ for products	-962.45	1.7
$\Delta H^{\circ}_{f298}[A\ell B_{2.215}(c)]$	- 16.2	2.9

Since analytical methods for determining boron and aluminum in aluminum diboride are good to 0.1 percent, the fact that the percent boron was found to be 2.5 percent in excess of the theoretical value and the percent aluminum was found to be 2.5 percent below the theoretical value in the aluminum diboride sample, we felt a non-stoichiometric treatment of the data was a preferred representation.

Assuming that average analytical errors for boron and aluminum in $A\ell B_2$ are each ±0.1 percent, if the boron analysis is high by this amount and the aluminum analysis low, a boron to aluminum ratio of 2.01 to 1 is obtained. An error of this type will lead to a maximum error of 2.0 kcal mole^{-1} in the heat of combustion.

In dealing with the impurities in α- and γ-aluminum dodecaboride we chose treatment (4) as the best representation for the data. The heats of formation of α-$A\ell B_{12}$ and γ-$A\ell B_{12}$ have been calculated from the data in Tables 11 and 12, and our data on aluminum fluoride [2] and boron trifluoride according to reactions (8) and (9):

$$\alpha\text{-}A\ell B_{12}(c) + \frac{39}{2} F_2(g) = A\ell F_3(c) + 12BF_3(g) \qquad (8)$$

$$\gamma\text{-}A\ell B_{12}(c) + \frac{39}{2} F_2(g) = A\ell F_3(c) + 12BF_3(g) \qquad (9)$$

We find for $\Delta H^{\circ}_{f298}[\alpha\text{-Al}B_{12}(c)]$, -61.5 kcal mole^{-1} and for $\Delta H^{\circ}_{f298}[\gamma\text{-Al}B_{12}(c)]$, -39.1 kcal mole^{-1}, respectively. The data used to calculate the heats of formation and corresponding over-all experimental errors for α-AlB_{12} and γ-AlB_{12} are shown in Tables 22 and 23.

Table 22

Heat of Formation of α-Aluminum Dodecaboride

Type of Data	Heat Data kcal mole^{-1}	Over-all Experimental Error, kcal mole^{-1}
ΔH°_{c298} $[\alpha\text{-Al}B_{12}(c)]$	-3560.7	10.7
$\Sigma\Delta H^{\circ}_{f298}$ for products	-3622.2	2.1
ΔH°_{f298} $[\alpha\text{-Al}B_{12}(c)]$	-61.5	10.9

Table 23

Heat of Formation of γ-Aluminum Dodecaboride

Type of Data	Heat Data kcal mole^{-1}	Over-all Experimental Error, kcal mole^{-1}
ΔH°_{c298} $[\gamma\text{-Al}B_{12}(c)]$	-3583.1	12.9
$\Sigma\Delta H^{\circ}_{f298}$ for products	-3622.2	2.1
ΔH°_{f298} $[\gamma\text{-Al}B_{12}(c)]$	-39.1	13.1

Because of the relatively large amounts of impurities in the aluminum borides studied, we have attempted to estimate limits to the uncertainties introduced into the calculated heats of formation by the lack of knowledge of the exact nature of the impurities. This has been done by using the composition of the samples listed in Tables 16, 17 and 18 as columns (1), (2), (3) and (4), respectively.

The heats of formation of aluminum diboride, α- and γ-aluminum dodecaborides, calculated by assuming these distributions of non-metallic impurities between aluminum and boron, are shown in Table 24. The values listed for treatments (1), (2) and (4) differ from those obtained by treatment (3) in that they refer to the stoichiometric rather than non-stoichiometric compounds. Treatments (3) and (4) are similar in that they assume that the distribution of non-metallic impurities is proportional to either the non-stoichiometric or stoichiometric number of moles of aluminum and boron present in the sample. Inpsection of Table 24 shows that the heats of formation calculated using a given treatment does not vary considerably from another treatment for the same sample. The maximum variation in ΔH°_{f298} appears to be 3.5 kcal mole^{-1} in the case of α-$A\ell B_{12}$ calculated using treatments (1) and (3). It is evident that an indefinite number of distributions other than the ones selected are possible. Because of the manner of assigning the compositions used in treatments (1) and (2), we feel that the heats of formation derived by using them represent approximate extremes to the values that would be obtained using any accessible composition.

Table 24

Dependence of the Derived Heats of Formation of the Aluminum Borides upon the Method of Treatment of Impurities

Assumed Sample Composition	Treatment (1) kcal mole^{-1}	Treatment (2) kcal mole^{-1}	Treatment (3) kcal mole^{-1}	Treatment (4) kcal mole^{-1}
$A\ell B_2$	-15.9	-15.8		-16.1
$A\ell B_{2.215}$			-16.2	
α-$A\ell B_{12}$	-65.0	-61.9		-61.5
α-$A\ell B_{11.96}$			-61.3	
γ-$A\ell B_{12}$	-39.4	-39.0		-39.1
γ-$A\ell B_{12.57}$			-37.9	

In examining the heat of formation data on α-$A\ell B_{12}$ and γ-$A\ell B_{12}$ we find that the γ-phase is 22 kcal mole^{-1} less negative than the α-phase. Inasmuch as approximately the same heat value is obtained for the heat of combustion of α-$A\ell B_{12}$ no matter what method of preparation is used in making the pellet, leads us to feel that premature reaction of α-$A\ell B_{12}$ is not the reason for this difference in the heat data. Inspection of areas which are possible sources of error shows that small errors in the analysis of boron and aluminum in AlB_{12} can seriously affect the calculated heat data. We estimate that the error in the aluminum analysis is about ±0.1 percent and that in the boron analysis about ±0.2 percent. If the boron analysis was 0.2 percent higher than the theoretical value and the aluminum analysis 0.1 percent lower than the theoretical value, a stoichiometry of $AlB_{12.10}$ would be obtained. If, for example, our α-AlB_{12} sample had a molar ratio of boron to aluminum of exactly 12 to 1, and we assume the same for the γ-AlB_{12} sample, but in reality its true stoichiometry was γ-$AlB_{12.10}$, then the calculated heats of combustion and formation would differ from each other by 25 kcal mole^{-1}. This illustrates that although the difference we observe in the calculated heat of combustion and formation of our α-AlB_{12} and γ-AlB_{12} samples is seemingly large, 22 kcal mole^{-1}, it is within the limits of the experimental error that one could expect from this type of error in the analysis of the AlB_{12} samples.

Another source of error could be the fact that the sum of the aluminum, boron and impurity analyses for γ-AlB_{12} come to 97.29 percent, leaving 2.71 percent of the sample unaccounted for. This implies that either certain elements were overlooked in our study of the composition of this sample, or the refractory nature of γ-AlB_{12} has resulted in an incomplete analysis of certain elements.

The supplier of γ-AlB_{12} stated that the sample was not a single phase material but had about 10 percent of the α-phase syntactically intergrown in it. The two phases are extremely similar from a structural standpoint and it is difficult to envision why there should be a large difference in the heats of formation of the 90% γ- 10% α-phase, and the α-phase itself.

From the study of Matkovich et al. [57] in dealing with the preparation of the aluminum borides, we noticed that α-AlB_{12} appears more stable than γ-AlB_{12} since slow cooling of an aluminum-boron melt (20% Al, 80% B by weight) from 1700°C would result in the formation of both α- and γ-phases, while rapid cooling gave only the α-phase. This indicates that the α-phase should have a more negative heat of formation than the γ-phase, however the magnitude expected would be somewhat less than the 22 kcal mole^{-1} observed from our investigation.

10. Conclusion

The heats of combustion of boron, boron carbide, graphite, aluminum diboride, α-aluminum dodecaboride and γ-aluminum dodecaboride were determined by means of fluorine bomb calorimetry. From the experimental data appropriate heats of formation were calculated and are shown in Table 25 along with the over-all experimental error.

Table 25

Summary of Heat of Formation Data

Substance and State	ΔH°_{f298} kcal mole^{-1}	Over-all Experimental Error kcal mole^{-1}
BF_3(g)	-271.82	0.38
CF_4(g)	-222.87	0.13
B_4C(c)	- 19.5	4.6
$A\ell B_{2.215}$(c)	- 16.2	2.9
α-$A\ell B_{12}$(c)	- 61.5	10.9
γ-$A\ell B_{12}$(c)	- 39.1	13.1

11.0 References

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