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WADD TR 60-782, PT VIII

CATALOGED BY ASTIA 277796  
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## VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES

### PART VIII. MASS SPECTROMETRIC STUDY OF GASEOUS SPECIES IN THE SYSTEM BORON-CARBON

TECHNICAL DOCUMENTARY REPORT No. WADD 60-782  
PART VIII

APRIL 1962

DIRECTORATE OF MATERIALS AND PROCESSES  
AERONAUTICAL SYSTEMS DIVISION  
AIR FORCE SYSTEMS COMMAND  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Project No. 7350, Task No. 735001

(Prepared under Contract No. AF 61(052)-225  
by the Universite Libre de Bruxelles, Brussels, Belgium;  
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## FOREWORD

This report was prepared by the University of Brussels, Belgium, under USAF Contract No. AF61(052)-225. The contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735001, "Non-graphitic." The work was administered under the direction of the Directorate of Materials and Processes, Deputy Commander/Technology, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. Mr. F. W. Vahldiek was the project engineer.

This report covers work conducted from March 1961 to March 1962.

WADD Technical Report 60-782, Parts I, II, III, V, VI have already been published. Part VII is in preparation, with Part IV to follow when it becomes available.

The authors wish to thank Professor P. Goldfinger for his interest and encouragement. Gifts of  $B_4C$  by Norton (Belgium) and research grade  $B_4C$  by the Carborundum Company are gratefully acknowledged.

### ABSTRACT

The molecules BC, B<sub>2</sub>C and BC<sub>2</sub> have been identified. Their atomization energies have been measured to be  $D_0^\circ(\text{BC}) = 105 \pm 10$ ;  $D_0^\circ(\text{B}_2\text{C}) = 260 \pm 10$ ;  $D_0^\circ(\text{BC}_2)^\circ = 302 \pm 10$  kcal/mole.

### PUBLICATION REVIEW

This technical documentary report has been reviewed and is approved.

FOR THE COMMANDER:



W. G. RAMKE  
Chief, Ceramics and Graphite Branch  
Metals and Ceramics Laboratory  
Materials Central

## MASS SPECTROMETRIC STUDY OF GASEOUS SPECIES

### IN THE SYSTEM BORON-CARBON\*

Molecules of high stability are known to exist in the vapors in equilibrium with Boron<sup>(1)</sup>, Carbon<sup>(2-5)</sup>, Silicon Carbide<sup>(6-7)</sup> and several metallic carbides and metal-Carbon systems<sup>(8-9)</sup>. It was therefore of interest to study the vapor in equilibrium with the Boron-Carbon system.

The experiments were performed with a 20 cm, 60° sector single focusing mass spectrometer, equipped with a secondary electron multiplier. The general arrangement is that described previously<sup>(10)</sup>, except that differential pumping between the Knudsen cell and the ionization source compartments was added. The Knudsen cells made from high purity graphite, wrapped in a tantalum sheet and surrounded by tantalum radiation shields, were heated by electron bombardment. Their temperature was measured with an optical pyrometer. The area of the effusion hole was varied from  $2 \times 10^{-3}$  to  $8 \times 10^{-2}$  cm<sup>2</sup>.

Large and small (milligram) samples of amorphous boron, intimate mixtures of powdered graphite and amorphous boron

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Manuscript released by the authors March 1962 for publication as an ASD Technical Documentary Report.

and research grade boron carbide were studied in the temperature range 1780 - 2500°K. Systematic variations in ionic intensities indicating reaction between boron and graphite were observed at approximately 2300°K.

The gaseous species observed were B, C, C<sub>2</sub> and C<sub>3</sub>, BC, B<sub>2</sub>C and BC<sub>2</sub>. All of these species were identified<sup>(11)</sup> from their masses, isotopic distribution, appearance potential and intensity distribution in the molecular beam. The appearance potential of boron, determined by the linear extrapolation method, using mercury to calibrate the energy scale, agreed with the known ionization potential<sup>(12)</sup>. Approximate appearance potentials of BC, B<sub>2</sub>C and BC<sub>2</sub>, subsequently measured relative to that of boron, were 10.0, 10.2 and 10.4 ± 0.6 ev respectively. Within experimental error the appearance potentials of C, C<sub>2</sub> and C<sub>3</sub> measured here agreed with those determined earlier<sup>(2,5)</sup>. The ionization efficiency curve for the BC<sup>+</sup> ion showed fragmentation to contribute appreciably to the intensity measured above 17 ev. The data were therefore taken with low energy electrons.

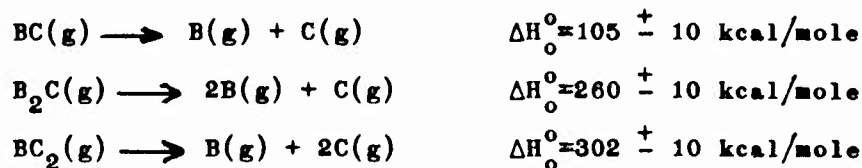
Relative partial pressures were deduced from the experimental ion intensities using corrections for differences in ionization cross section<sup>(13)</sup>, in energy of the ionizing electrons and in secondary electron multiplier efficiency. Typical

relative pressures for gaseous B, B<sub>2</sub>C and BC<sub>2</sub> over amorphous boron and graphite at 2167°K were  $1/10^{-2}/5 \times 10^{-2}$ . Over B<sub>4</sub>C + graphite, the ratio  $P_{BC}/P_B$  was  $7 \times 10^{-4}$  at 2400°K. Enthalpy changes,  $\Delta H_o^\circ$ , were calculated for the reactions  
 $BC(g) \longrightarrow B(g) + C(s)$ ,  $B_2C(g) \longrightarrow B(g) + B(s) + C(s)$ ,  
 $B_2C(g) \longrightarrow B(g) + 1/4 B_4C(s) + 3/4 C(s)$  and  
 $BC_2(g) \longrightarrow B(g) + 2C(s)$  using the formula:

$$\Delta H_o^\circ = -RT \ln K - T\Delta \left[ F_T^\circ - H_o^\circ/T \right]$$

where K is the equilibrium constant and  $F_T^\circ - H_o^\circ/T$  the free energy function. For the above reactions the equilibrium constants are dimensionless and were hence derived from the relative corrected intensities without absolute pressure calibration. Values of  $F_T^\circ - H_o^\circ/T$  for amorphous boron were taken from Wise and Margrave<sup>(14)</sup>, for graphite and gaseous boron from Stull and Sinke<sup>(15)</sup>, and for boron carbide from Margrave<sup>(16)</sup>. The free energy functions of the molecules BC, B<sub>2</sub>C and BC<sub>2</sub> were estimated. The enthalpy changes obtained for the above reactions were -64, -38, -41 and -38 kcal/mole respectively.

Whence the atomization energies:



When hexagonal SiC was added to the system, the molecules BSi and BCSi were identified in addition to the molecules characteristic of the B-C and Si-C systems<sup>(6-7)</sup>. The molecule BSi<sub>2</sub> was tentatively identified. From the present data atomization energies of 70 and 250 kcal/mole were derived for BSi and BCSi respectively.

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| <p>Aeronautical Systems Division, Dir/Materials and Processes, Metals and Ceramics Lab, Wright-Patterson AFB, Ohio<br/>Rpt Nr WADD TR 60-782, Pt VIII. VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE: Mass Spectrometric Study of Gaseous Species in the System Boron-Carbon. 7 p. incl 16 refs.</p> <p>Unclassified report</p> <p>The molecules BC, B<sub>2</sub>C, and BC<sub>2</sub> have been identified. Their atomization energies have been measured to be D<sub>0</sub>(BC) = 105 ± 10; D<sub>0</sub>(B<sub>2</sub>C) = 260 ± 10; D<sub>0</sub>(BC<sub>2</sub>)<sup>0</sup> = 302 ± 10 kcal/mole.</p> <p>( over )</p> | <p>1. Boron-Carbon system.<br/>2. Mass spectrometric study</p> <p>I. AFSC Project 7350, Task 735001<br/>II. Contract AF61(052)-225.</p> <p>III. University of Brussels, Belgium<br/>IV. G. Verhaegen et al<br/>V. Aval fr OTS<br/>VI. In ASTIA collection</p> | <p>Aeronautical Systems Division, Dir/Materials and Processes, Metals and Ceramics Lab, Wright-Patterson AFB, Ohio<br/>Rpt Nr WADD TR 60-782, Pt VIII. VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE: Mass Spectrometric Study of Gaseous Species in the System Boron-Carbon. 7 p. incl 16 refs.</p> <p>Unclassified report</p> <p>The molecules BC, B<sub>2</sub>C, and BC<sub>2</sub> have been identified. Their atomization energies have been measured to be D<sub>0</sub>(BC) = 105 ± 10; D<sub>0</sub>(B<sub>2</sub>C) = 260 ± 10; D<sub>0</sub>(BC<sub>2</sub>)<sup>0</sup> = 302 ± 10 kcal/mole.</p> <p>( over )</p> | <p>1. Boron-Carbon system.<br/>2. Mass spectrometric study</p> <p>I. AFSC Project 7350, Task 735001<br/>II. Contract AF61(052)-225.</p> <p>III. University of Brussels, Belgium<br/>IV. G. Verhaegen et al<br/>V. Aval fr OTS<br/>VI. In ASTIA collection</p> |
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