FOREWORD

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ABSTRACT

The systems B-C and B-C-Si were investigated mass-spectrometrically. The atomication energy of the newly identified molecules BC_2, B_2C, BCSi, BSi_2, BC and BSi are 294, 254, 247, 174, 107 and 68 kcal/mole respectively. The atomization energy of SiC_2, Si_2C and SiC were redetermined.

This technical documentary report has been reviewed and is approved.

W. G. RAMKE
Chief, Ceramics and Graphite Branch
Metals and Ceramics Division
Air Force Materials Laboratory

SUMMARY

The vaporization behavior of the system boron-carbon and boron-carbon-silicon has been studied with a mass spectrometer. In addition to the gaseous species characteristic of graphite, silicon carbide and boron, the molecules BC_2, B_2C, BCSi, BSi_2, BC and BSi were identified and their atomization energy measured. The values are: 294, 254, 247, 174, 107 and 68 kcal/mole respectively. The atomization energy of SiC, Si_2C and SiC_2 have been redetermined.

INTRODUCTION

An increased interest has recently been developed in the properties of borides and carbides. Mass spectrometric studies of the vapor phases in equilibrium with carbon(1-4) and with several carbides(5-8) have shown the existence of numerous di and polyatomic molecules of great interest and stability. Similar studies of boron(9,10) had shown the gas phase to be essentially monoatomic. Furthermore until now no gaseous borides have been detected.

It was therefore of interest to study the system boron-carbon. A preliminary report of the gaseous species identified was already given(11), while a determination of the heat of sublimation of boron, $\Delta H^o_0(B)$ = 128.0 kcal/mole and of the heat of formation of boron carbide, $\Delta H^o_{298}(B_4C)$ = 13.6 kcal/mole was performed(10) since these quantities were required in the

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evaluation of the stability of the gaseous molecules. These stabilities, as well as those of a number of molecules in the system Boron-Carbon-Silicon are discussed in detail here.

EXPERIMENTAL

The experiments were performed with a 20 cm radius of curvature, 60° sector single focusing spectrometer equipped with a secondary electron multiplier, described previously(12). Differential pumping between Knudsen cell and ionization source compartment was added(11) to reduce the effect of oven outgassing on the ionization source compartment and the analyzer tube pressures. A pressure gradient of more than a factor ten could be maintained between Knudsen cell and ionization source compartments.

The Knudsen cells, made from high purity graphite wrapped in tantalum sheet and surrounded by tantalum radiation shields, were heated by electron bombardment. Their temperature was measured by sighting into a small threated hole drilled in the bottom of the graphite cell with a Leeds and Northrup disappearing filament optical pyrometer. Corrections for window absorption were made according to calibrations(12). The effusion hole area of the cells was varied from 1.96 10^{-3} to 7.06 10^{-2} cm^2, which corresponds to sample area to effusion orifice area ratios of 150 and 5 respectively.

Samples of powdered amorphous[*] boron or research grade boron carbide were used; in some experiments crushed hexagonal SiC crystals were added. The vaporization behavior of all systems was studied in the temperature range 1780-2500°K.

The gaseous species effusing from the cell were made to pass, after severe collimation, through the ionization chamber of the spectrometer where they were ionized by a 3μA electron beam of energy ranging between 6 and 25 volts. The ions thus formed were accelerated to 2000 volts before entering the analyzer tube and to 4500 volts before impinging upon the secondary electron multiplier.

RESULTS

a) Identification of Species.

In addition to gaseous species previously observed in the carbon(1-4), boron(9-10) and silicon carbide(6) systems, the molecules BC, BSi, BC_2, BCSi, BSi_2 and B_2C were identified in this study. Their identification resided in the measurement of their mass, their isotopic distribution, their intensity profile in the molecular beam and their appearance potential.

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[*] X-ray examination showed that the boron may in part have been microcrystalline. For the evaluation of the thermochemical data, thermal functions(13,14) for crystalline boron were used, it being considered that at the temperatures of the investigation, the transformation of amorphous boron would have been rapid.

The observed isotopic distributions corresponded within 5% with literature values(15). The intensity profiles indicated all neutral species except C, C_2 and C_3 to originate from the effusion orifice; these species originated in part from the effusion orifice and in part from the surface of the cell. Appearance potentials were measured relative to that of atomic boron and silicon after ascertaining that B^+ and Si^+ did not result from fragmentation by comparing their appearance potentials with that of a residual gas. Values thus measured are given in Table I. The appearance potential of BSi_2^+ could not be measured due to its small intensity; the value given in Table I was estimated by analogy with similar molecules. The appearance potentials measured here for the previously observed gaseous species agreed with the values given in the literature(6,16), except for C_2 and C_3 for which values about 0.7 eV lower than those reported(4) were deduced. It should be noted however that this difference is largely due to different extrapolations of similar ionic intensity vs ionizing electron energy plots. For both C_2 and C_3 these plots show a marked curvature for low ionizing electron energies instead of the more usual linear dependance. This apparently can be attributed to low-lying excited states in the parent molecules as well as in the molecular ions(17-19). The appearance potential curves of BC^+ and SiC^+ deserve closer attention. Figure 1 shows the ionic intensity of BC^+ and SiC^+ as a function of ionizing electron energy. As can be seen, most of the ionic intensity measured above 17 volts for BC^+ and 15 volts for SiC^+ results from fragmentation of the much more abundant species BC_2 and B_2C, and SiC_2 and Si_2C respectively. The ionic intensity of BC^+ was therefore measured at 16 volts and that of SiC^+ at 14 volts. It may be noted that the difference between the appearance potentials of the parent and the fragment ions is in agreement with the bond energies of the fragmented species (Table 5). Because of the well known uncertainties in this type of measurement however the stability of BC_2, B_2C, SiC_2 and Si_2C was not derived in this way but rather from thermochemical relations based on their partial pressures as discussed below.

b) Pressure Data

Partial pressures were derived from the relation(20)

$$P = IT(V_M-A)/S\sigma\gamma(E-A)$$

where P is the partial pressure, I the ionic intensity in arbitrary units, T the temperature of the effusion cell, A the appearance potential, S the sensitivity factor, σ the relative cross section at the maximum of the ionization efficiency curve, γ the relative secondary electron multiplier gain, E the energy of the ionizing electrons at which the species was measured and V_M the energy of the ionizing electrons for which the ionization cross section reaches a constant value.

The sensitivity factor S was derived either from a quantitative vaporization pressure calibration with silver in the same experiment made immediately preceding the measurement of the intensity of the species of interest or from calibrations with the silicon(21) and/or boron(10) partial pressures at the beginning of the experiments, assuming the silicon carbide and/or boron activities to be unity. The ratio σ_B/σ_{Ag} was measured separately(10). Results using either pressure standard agree within experimental error.

Relative ionization cross sections were taken from Otvos and Stevenson(22) for B, C and Si. Cross sections for molecules were estimated following the additivity rules proposed by those authors(22). The relative gain of the secondary multiplier used in these experiments has been calibrated previously as a function of mass(12). Molecular effects on the first dynode of the multiplier were taken into account using the formula proposed by Stanton, Chupka and Inghram(23). All values used are presented in Table 1.

Table 2 gives partial pressure measurements of the species observed in this study. In the second column are given the pressure standards used for each experiment and in the third column the temperatures arranged in chronological order within each experiment. The pressures given are believed to be correct within a factor of 2 or better. For the reason given above C^+, C_2^+ and C_3^+ ion intensities were not used to obtain pressures for the corresponding molecules nor were their known pressures(4) used as standards.

There seemed to be an influence of the effusion hole area on the partial pressure of BC_2 and B_2C over the system boron-carbon (as well boron + graphite as boron carbide + graphite). The observations are presented graphically in figure 2 which gives the equilibrium constant $K = P_B/P_{BC_2}$ at 2000 and 2200°K for the reaction $BC_2(g) \rightarrow B(g) + 2C(\text{graphite})$, as a function of the ratio of effusing and vaporizing areas, s and S respectively. S was taken as the cross sectional area of the cell. The values of K are given with error limits corresponding to the standard statistical deviations.

The same and previous experiments(10) showed the boron pressure itself to be independent of the relative effusion area. The variation in the equilibrium constant thus gives the relative variation in BC_2 pressure.

Less extensive data obtained for the boron-silicon carbide-graphite system would seem to indicate that similar effects are largely attenuated in the latter system.

If the equilibrium constant is represented by the relation $K=K^\circ(1+s/xS)$, chosen by analogy with the relation $P^\circ=P(1+s/\alpha S)$, (P°= equilibrium pressure, P= measured pressure) by which evaporation coefficients α are often evaluated, a value $x=0.17$ is obtained. For B_2C a similar treatment of the equilibrium constant $B_2C(g) \rightarrow B(g)+B(\text{condensed})+C(\text{graphite})$ is much less clear.

The pressure data used to calculate the stability of BC_2 and B_2C were taken from the experiment with the lowest value of s/S (Figure 2). These data were judged to approach equilibrium conditions (extrapolated value in fig.2) sufficiently.

c) Atomization Energies.

The atomization energy of each specie was calculated by the third law method:

$$\Delta G^o_T = -RT \ln K = \Delta H^o_o + T\Delta(G^o_T - H^o_o)/T$$

The use of this relation necessitated the estimation of the free energy functions of all newly identified molecules. These were estimated by analogy with the known or previously estimated values for similar molecules. The values thus obtained were corrected when judged necessary for differences in effective quantum weights and symmetry numbers. Table 3 summarizes the approach used and Table 4 the values of the free energy functions derived from the usual statistical thermodynamic formulae.

It should be noted that the free energy function of BSi_2 was obtained by analogy with a value of the free energy function of Si_2C estimated previously(6) on the grounds of a Si-Si-C structure rather than with the value used here(24) estimated on the basis of a Si-C-Si structure.

In order to reduce experimental errors, the chemical equilibria used to calculate the stability of the species were chosen so as to be independent of an absolute value of the pressure and thus of a possible variation of the sensitivity factor during the course of an experiment. Table 5 gives the chemical equilibria, the corresponding mean enthalpy change with statistical deviation, the number of experimental points and the atomization energy of the gaseous species considered with estimated error limits.

The uncertainties quoted in Table 5, column 3 are 95% probability limits ($2\sigma=2\left(\sum_n\left(\frac{\varepsilon}{n-1}\right)^2\right)^{1/2}$), ε is the difference between the experimental value and the mean and n is the number of experimental points). All points from different sets of experiments were considered as belonging to the same experiment. If instead the error had been separately calculated for each set of experiments the apparent statistical error limits would have been somewhat lessened, but it was felt that such a treatment would not give a true picture of the actual spread in the results within each set of experiments. Furthermore, except for BC_2 and B_2C mentioned above, there seemed to be no systematic differences between results obtained from different experiments.

In the last column of Table 5 are given the proposed atomization enthalpies of the molecules cited in the first column. The error limits given there take into account, in addition to the statistical deviations, the spread in the atomization energies obtained from different chemical equilibria. (Table 5, column 5), and possible systematic errors due to temperature measurements (1%), uncertainties in relative ionization cross-sections and their dependance on ionizing electron energy as written in Equation 1 (60%), and uncertainties in the estimated free energy function. These have often been discussed previously(29,30); the greatest of them arises from the electronic partition function. An overall absolute uncertainty of 2.5 entropy units has been estimated for all molecules. It has been assumed for the calculation that these possible errors are independent of each other.

DISCUSSION

a) Effect of Relative Effusion Hole Area.

It is difficult to give an unambiguous interpretation of the meaning of this effect, which seems nevertheless related to the molecule BC_2. A previous determination of the boron pressure(10) showed indeed that this element did not react with graphite below 2300°K and that its measured pressure was independent of the ratio of the areas of the effusion orifice and of the subliming surface. Two extreme cases can then be envisaged. In one, gaseous boron would initially react with graphite to form a boron carbide layer which hinders further reaction. The reaction $B(g)+2C(\text{graphite}) \rightarrow BC_2(g)$ would then be controlled by diffusion through this layer. In the other case, gaseous boron impinging on the graphite surface of the cell would be reflected without reacting. The collision efficiency of gaseous boron with graphite to form either condensed B_4C or gaseous BC_2 would thus be low. The present experiments would then give a measure of the collision efficiency in the latter reaction, $x=0.17$. This efficiency of 0.17 would mean that on the average 1 out of 6 boron atoms which under conditions of thermodynamic equilibrium should give rise to BC_2 does in fact do so. It is perhaps noteworthy in connection with the latter interpretation that atomic carbon and C_3 molecules, have reflexion coefficients of 0.6 and 0.9 respectively on a polycrystalline graphite surface at 2000°K(31).

b) Atomization Energies.

The values obtained here for the atomization energy of SiC_2, Si_2C and SiC can be compared with those from a previous determination(6) 307, 250 and 103 kcal/mole respectively. The difference for Si_2C mainly results from a different estimation of the free energy function of this molecule as mentioned above. The 4 kcal/mole differences measured for SiC_2 and SiC are within experimental uncertainty, especially in the case of SiC.

The atomization energies of the molecules BC_2, B_2C, BCSi and BSi_2 show these species to be very strongly bonded. In addition, these molecules, as well as the triatomics SiC_2, Si_2C, Si_3 and C_3, are more stable than predicted by summing "bond energies" ascribed to the individual bonds. This "extra" energy or "resonance energy"(32) has been calculated by comparing the observed atomization energies to the sum of the D_0^o for the corresponding pairs of diatomic molecules and presumably is due to partial delocalization of the bonding electrons. The data and calculated values of the "resonance energies" are presented in Table 6.

The results show that all these molecules except possibly C_3 have about 20% extra binding energy. This number has been used to calculate the atomization energy of B_2Si and B_3, species not observed in this study. Values of 160 and 155 kcal/

mole were thus obtained for B_2Si and B_3 respectively. It should be noted however that since all of the observed triatomics are believed to have a central Group IV atom, the application of this correlation to B_3 may be less valid. One would guess the value so obtained to be a maximum value.

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TABLE 1.

Relative Ionization Cross Sections (σ), Relative Secondary Electron Multiplier Yields (γ) and Appearance Potentials (A.P.)

Species	σ	γ	A.P. (eV)	Species	σ	γ	A.P. (eV)
B	5.02	1.05	8.3	BC_2	13.3	1.17	10.7
Si	14.4	0.97	8.1	B_2C	14.2	1.18	10.7
BC	9.18	1.13	10.5	BCSi	23.6	1.03	9.9
BSi	19.4	1.04	7.8	BSi_2	33.8	0.97	(9)
SiC	18.6	1.04	9.0	SiC_2	22.7	1.06	10.2
Si_2	28.8	0.97	7.3	Si_2C	32.9	0.97	9.1

TABLE 2. Observed Partial

Exp	Pressure calibration	T°K	P_B	P_{BC}	P_{BC_2}	P_{B_2C}	P_{Si}	
0711	B	2345	$1.7\ 10^{-5}$	$8.3\ 10^{-9}$	-	-	-	1
		2405	$1.4\ 10^{-4}$	$1.0\ 10^{-7}$	-	-	-	2
0721	B	2268	$1.1\ 10^{-5}$	$7.2\ 10^{-9}$	- -	-	-	3
		2323	$1.9\ 10^{-5}$	$1.3\ 10^{-8}$	-	-	-	4
		2346	$2.3\ 10^{-5}$	$1.9\ 10^{-8}$	-	-	-	5
		2303	$5.0\ 10^{-6}$	$3.6\ 10^{-9}$	-	-	-	6
0707	B	2188	$1.4\ 10^{-5}$	-	$4.0\ 10^{-7}$	$1.0\ 10^{-7}$	-	7
		2286	$2.8\ 10^{-5}$	-	$1.5\ 10^{-6}$	$2.0\ 10^{-7}$	-	8
0712	Ag	2167	$3.9\ 10^{-6}$	-	$1.1\ 10^{-7}$	$3.8\ 10^{-8}$	-	9
		2228	$1.3\ 10^{-5}$	-	$7.2\ 10^{-7}$	$2.1\ 10^{-7}$	-	10
		2199	$8.9\ 10^{-6}$	-	$4.6\ 10^{-7}$	$1.4\ 10^{-7}$	-	11
		2364	$6.6\ 10^{-5}$	-	$4.4\ 10^{-6}$	$9.6\ 10^{-7}$	-	12
0709	B, Si	2249	$5.8\ 10^{-6}$	-	$2.8\ 10^{-7}$	$6.3\ 10^{-8}$	$4.2\text{-}10^{-5}$	13
		2305	$1.2\ 10^{-5}$	-	$5.6\ 10^{-7}$	$1.2\ 10^{-7}$	$5.4\ 10^{-5}$	14
		2344	$2.1\ 10^{-5}$	-	$1.5\ 10^{-6}$	$3.5\ 10^{-7}$	$6.9\ 10^{-5}$	15
		2301	$1.0\ 10^{-5}$	-	$5.9\ 10^{-7}$	$6.8\ 10^{-8}$	$4.6\ 10^{-5}$	16
0719	B, Si	2150	$1.7\ 10^{-6}$	-	-	-	$1.3\ 10^{-5}$	17
		2166	$2.9\ 10^{-6}$	-	-	-	$3.2\ 10^{-5}$	18
0720	B, Si	2083	$2.0\ 10^{-6}$	-	$3.5\ 10^{-8}$	-	$3.5\ 10^{-5}$	19

	P_{BSi}	P_{BCSi}	P_{BSi_2}	P_{Si_2}	P_{SiC_2}	P_{Si_2C}	P_{SiC}
1	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-
11	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-
13	$3.2\ 10^{-9}$	$2.4\ 10^{-7}$	-	$3.2\ 10^{-8}$	$6.0\ 10^{-6}$	$1.5\ 10^{-6}$	$7.4\ 10^{-9}$
14	$5.6\ 10^{-9}$	$4.6\ 10^{-7}$	$1.1\ 10^{-9}$	$2.8\ 10^{-8}$	$1.3\ 10^{-5}$	$1.8\ 10^{-6}$	$1.2\ 10^{-8}$
15	$8.7\ 10^{-9}$	$7.8\ 10^{-7}$	$2.2.10^{-9}$	$5.5\ 10^{-8}$	$1.1\ 10^{-5}$	$4.7\ 10^{-6}$	$1.9\ 10^{-8}$
16	$2.0\ 10^{-9}$	$1.7\ 10^{-7}$	-	-	$8.1\ 10^{-6}$	$5.6\ 10^{-7}$	-
17	$2.5\ 10^{-9}$	$1.7\ 10^{-7}$	-	-	-	-	-
18	-	$3.5\ 10^{-7}$	$3.9\ 10^{-9}$	$3.5\ 10^{-8}$	$3.8\ 10^{-6}$	$2.4\ 10^{-6}$	-
19	$1.8\ 10^{-9}$	$2.2\ 10^{-7}$	$1.3\ 10^{-9}$	-	-	$3.8\ 10^{-6}$	-

Legend. The partial vapor pressures are given in atmospheres The experimental points within each experiment are given in chronological order.

TABLE 3.

Free Energy Functions: Basis of Estimation

Structure	Estimate of Free Energy Function	Effective Quantum Weight
Si-C	Estimated previously(6,24)	3
Si-Si	Spectroscopic Data(25,26)	3
B-C	Analogy with B_2(27), C_2(18), C_2^+(19)	10
B-Si	Analogy with B_2, Si_2, SiC	5
Si-C-C	Estimated previously(6,24)	1
Si-C-Si	Estimated previously(24)	1
B-C-C	Analogy with C_3(17)	6
B-C-B	Analogy with C_3	6
B-C-Si	Analogy with SiC_2	6
B-Si-Si	Analogy with Si_2C	6

TABLE 4. Free Energy Functions: Numerical Values

$$-\left(\frac{G^o_T - H^o_o}{T}\right) \text{ (cal/deg.mole)}$$

T Specie	2000	2100	2200	2300
B(28)	41.1	41.4	41.6	41.8
Si(28)	45.5	45.7	45.9	46.1
Si_2	62.9	63.3	63.7	64.1
SiC	60.6	61.0	61.4	61.8
BC	59.1	59.5	59.9	60.3
BSi	62.0	62.4	62.8	63.2
SiC_2	67.9	68.5	69.1	69.7
Si_2C	70.8	71.4	72.0	72.6
BC_2	66.7	67.3	67.9	68.5
B_2C	65.4	66.0	66.6	67.1
BCSi	71.5	72.1	72.7	73.3
BSi_2	76.7	77.4	78.1	78.7
C(graph)(28)	5.5	5.7	5.9	6.1
B(cryst)(13,14)	6.4	6.7	6.9	7.2
B_4C(cryst)(14)	29.5	30.6	31.7	38.8

TABLE 5. Atomization Energies

Molec.	Chemical Equilibrium	ΔH_0^o kcal/mole *	n°.exp pts.	ΔH_0^o atom	Proposed Value kcal/mole†
SiC	$SiC \rightleftarrows Si+(C)$	-62.2±0.5	3	107.4	107±5
SiC_2	$SiC_2 \rightleftarrows Si+2(C)$	-36.0±1.0	14	303.2	303±6
Si_2C	$Si_2C \rightleftarrows Si_2+(C)$	12.1±1.3	8	255.7	256±6
BC_2	$BC_2+Si \rightleftarrows B+SiC_2$ $BC_2 \rightleftarrows B+2(C)$	- 9.7±0.8 -44.7±1.8	11 14	293.5 294.5	294±6
BCSi	$BCSi+SiC_2 \rightleftarrows BC_2+Si_2C$ $BCSi+Si \rightleftarrows Si_2C+B$ $BCSi+Si \rightleftarrows Si_2+B+(C)$	8.8±1.4 - 9.0±1.7 3.0±1.6	9 12 9	249.4 246.7 246.6	247±6
B_2C	$B_2C+Si_2C \rightleftarrows 2BCSi$ $B_2C+Si \rightleftarrows BCSi+B$ $B_2C \rightleftarrows B+(B)+(C)$ $B_2C \rightleftarrows B+1/4(B_4C)+3/4(C)$	15.4±2.9 8.9±2.2 -39.9±2.4 -42.6±2.2	10 10 6 3	253.7 255.9 251.5 252.2	254±6
BSi_2	$BSi_2+SiC_2 \rightleftarrows BCSi+Si_2C$ $BSi_2+BC_2 \rightleftarrows 2BCSi$ $BSi_2+BC_2 \rightleftarrows B_2C+Si_2C$	-24.1±4.9 -27.5±4.7 -46.5±3.4	5 3 2	175.4 172.5 172.2	174±7
BSi	$BSi+Si \rightleftarrows B+Si_2$ $BSi+(C) \rightleftarrows BCSi$ $BSi+SiC_2 \rightleftarrows BC_2+Si_2$ $BSi+Si_2C \rightleftarrows BCSi+Si_2$	- 4.8±2.0 -10.6±1.8 5.1±1.3 2.4±1.6	6 6 3 7	69.2 66.8 69.9 67.7	68±6
BC	$BC \rightleftarrows B+(C)$	-63.4±4.1	12	106.2	106±7

* Statistical 95% probability error limits

† Error limits take into account possible systematic errors.

TABLE 6.

Molec.	D_o^o kcal/mole	Molec	ΔH^o_{oat} kcal/mole	$\frac{\Delta H^o_{oat}(XYZ)}{D_o^o(XY)+D_o^o(YZ)}$
C_2	144(18)	C_3	321(17)	1.12
Si_2	74(6)	Si_3	175(6)	1.18
BC	106	BC_2	294	1.18
SiC	107	B_2C	254	1.20
BSi	68	BCSi	247	1.16
B_2	65.5(10)	BSi_2	174	1.22
		Si_2C	256	1.20
		SiC_2	303	1.21

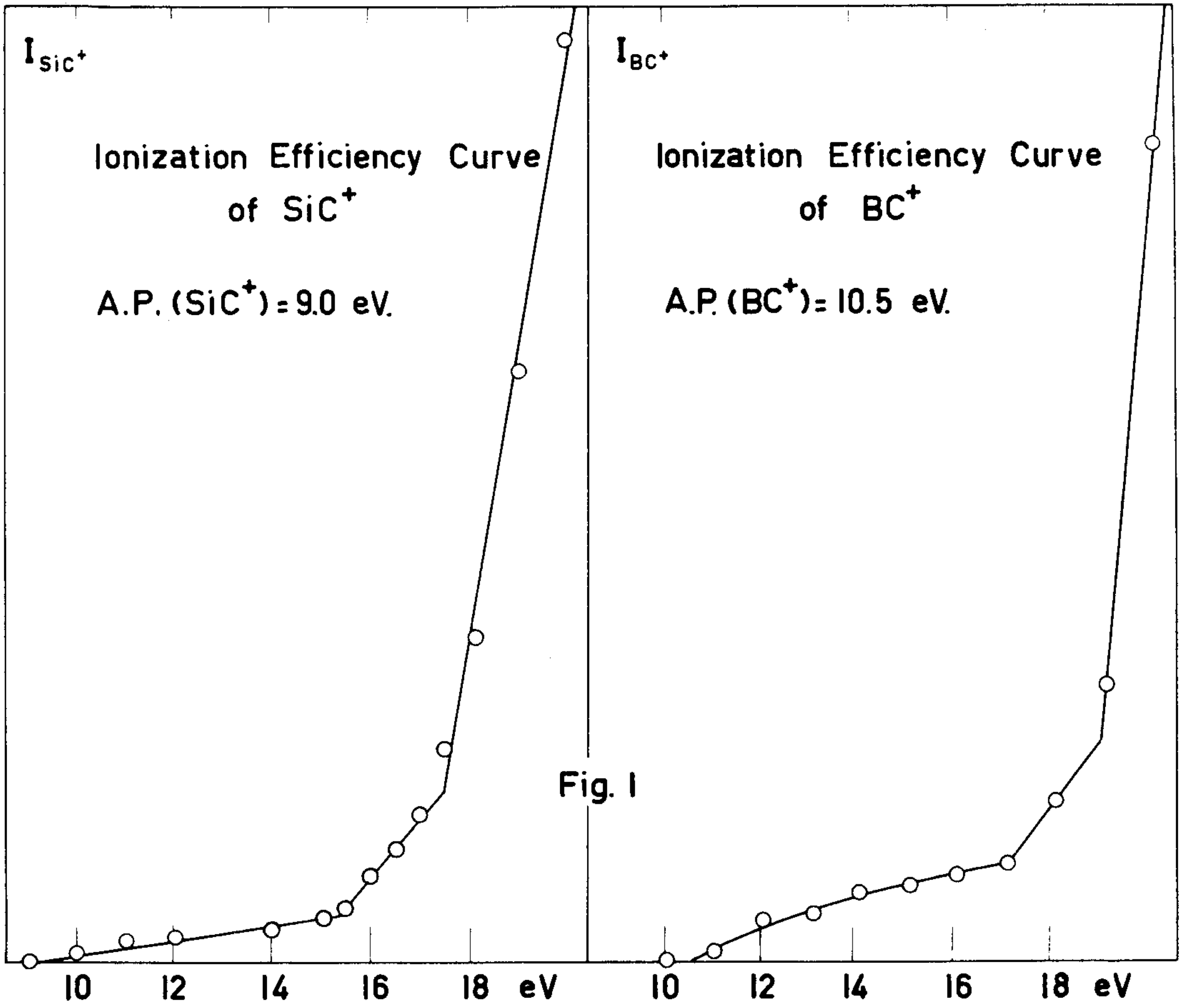
I_{SiC^+}
Ionization Efficiency Curve of SiC^+
A.P. (SiC^+) = 9.0 eV.
10
12
14
16
18
eV
I_{BC^+}
Ionization Efficiency Curve of BC^+
A.P. (BC^+) = 10.5 eV.
10
12
14
16
18
eV

Fig. 1

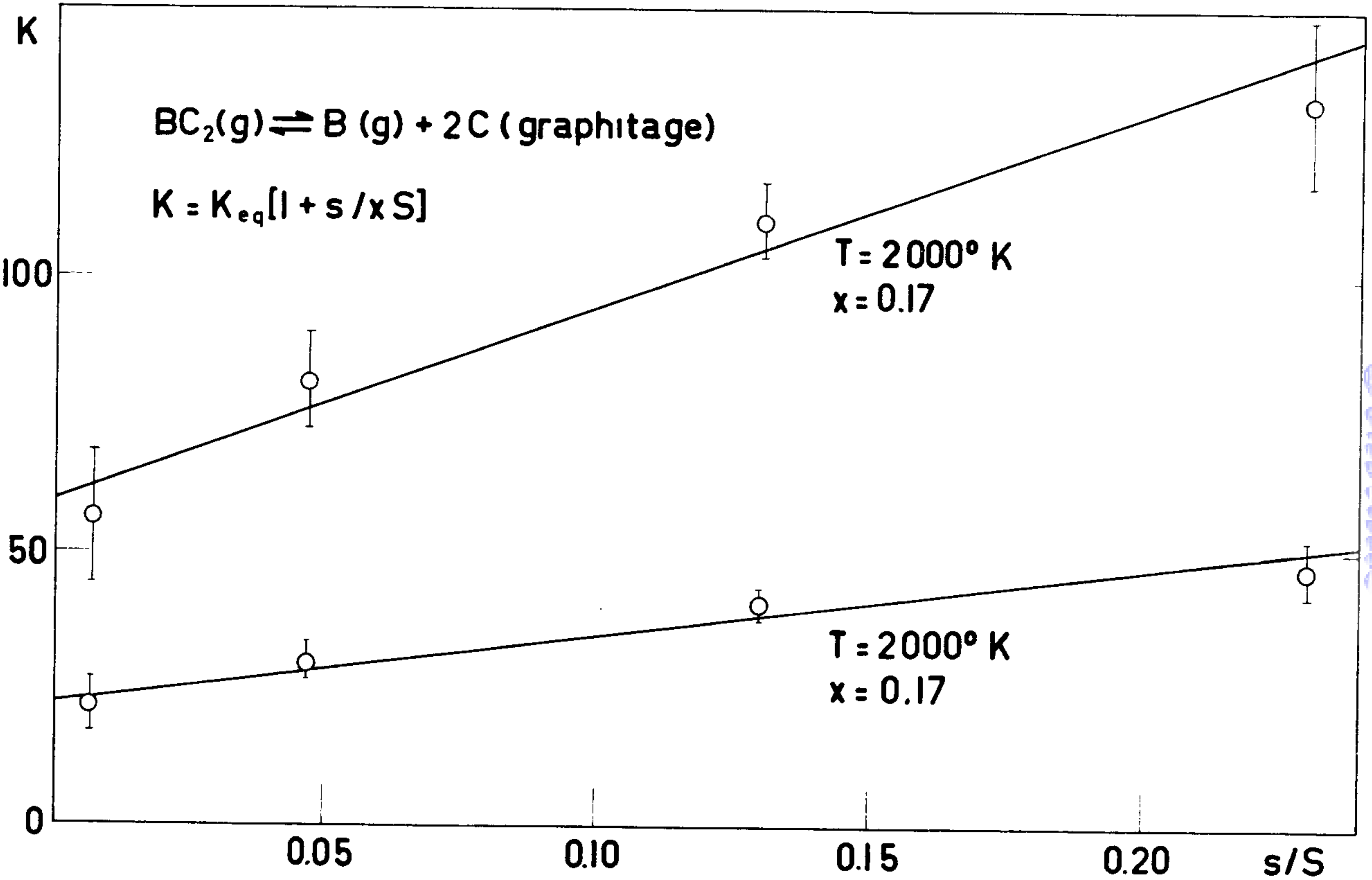
K
$BC_2(g) \rightleftharpoons B(g) + 2C$ (graphitage)
$K = K_{eq}[1 + s/xS]$
T = 2000° K
x = 0.17
T = 2000° K
x = 0.17
100
50
0
0.05
0.10
0.15
0.20
s/S

Fig 2

Legend to Figure 1.

Ionization efficiency curves of SiC^+ and BC^+. The first beeak in the ionization efficiency curve of SiC^+ at 15.3 eV is probably due to the process $Si_2C+e \rightarrow SiC^++Si+2e$ which from thermochemical data data and A.P.(SiC^+)= 9.0 eV yields 15.4 eV. The second, at 17.5 eV can be attributed to $SiC_2+e \rightarrow SiC^++C+2e$ which in the same manner yields 17.5 eV. This is in agreement with previous results(6,20). Similarly the breaks in the ionization efficiency curve of BC^+at 17.0 and 18.9 eV can be attributed to the processes $B_2C+e \rightarrow BC^++B+2e$ (17.0 eV) and $BC_2+e \rightarrow BC^++C+2e$ (18.7 eV) respectively.

Legend to Figure 2.

Effect of relative effusion area on the equilibrium constant (K) for the reaction $BC_2(g) \rightleftarrows B(g)+2C(\text{graphite})$. Points with $s/S = 0.007$ and 0.23 correspond to boron samples and points with $s/S = 0.047$ and 0.13 to boron carbide samples. The error limits given in the K values are standard statistical deviations.