CHEMISTRY

Mass Spectrometric Investigation of Gaseous Species in the System Boron–Carbon

MOLECULES of high stability are known to exist in the vapours in equilibrium with boron[1], carbon[2–5], silicon carbide[6,7] and several metallic carbides and metal–carbon systems[8,9]. It was therefore of interest to examine the vapour 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 was that described previously[10], 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 2×10^{-3} to 8×10^{-2} cm.^{2}.

Large and small (mgm.) samples of amorphous boron, intimate mixtures of powdered graphite and amorphous boron and research grade boron carbide were studied in the temperature-range 1.780–2.500° K. Systematic variations in ionic intensities indicating reaction between boron and graphite were observed at approximately 2,300° K.

The gaseous species observed were B, C, C_2 and C_3, BC, B_2C and BC_2. All these species were identified[11] 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[12]. Approximate appearance potentials of BC, B_2C and BC_2, afterwards 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_2 and C_3 measured here agreed with those determined earlier[2,5]. The ionization efficiency curve for the BC^+ ion showed fragmentation to contribute appreciably to the intensity measured above 17 eV. The measurements were therefore made with low-energy electrons.

Relative partial pressures were deduced from the experimental ion intensities using corrections for differences in ionization cross-section[13], in energy of the ionizing electrons and in secondary electron multiplier efficiency. Typical relative pressures for gaseous B, B_2C and BC_2 over amorphous boron and graphite at 2,167° K. were $1/10^{-2}/5 \times 10^{-2}$. Over B_4C + graphite, the ratio P_{BC}/P_B was 7×10^{-4} at 2,400° K. Enthalpy changes, ΔH_0^0, were calculated for the reactions $BC(g) \rightleftharpoons B(g) + C(s)$, $B_2C(g) \rightleftharpoons B(g) + B(s) + C(s)$, $B_2C(g) \rightleftharpoons B(g) + \frac{1}{4} B_4C(s) + \frac{3}{4} C(s)$ and $BC_2(g) \rightleftharpoons B(g) + 2C(s)$ using the formula:

$$\Delta H_0^0 = -RT \ln K - T\Delta [(F_T^0 - H_0^0)/T]$$

where K is the equilibrium constant and $(F_T^0 - H_0^0)/T$ the free-energy function. For these reactions the equilibrium constants are dimensionless and were hence derived from the relative corrected intensities without absolute pressure calibration. Values of $(F_T^0 - H_0^0)/T$ for amorphous boron were taken from Wise and Margrave[14], for graphite and gaseous boron from Stull and Sinke[15] and for boron carbide from Margrave[16]. The free-energy functions of the molecules BC, B_2C and BC_2 were estimated. The changes in enthalpy obtained for the above reactions were −64, −38, −41 and −38 kcal./mole respectively.

Whence the atomization energies:

$BC(g) \rightleftharpoons B(g) + C(g)$	$\Delta H_0^0 = 105 \pm 10$ kcal./mole
$B_2C(g) \rightleftharpoons 2B(g) + C(g)$	$\Delta H_0^0 = 260 \pm 10$ kcal./mole
$BC_2(g) \rightleftharpoons B(g) + 2C(g)$	$\Delta H_0^0 = 302 \pm 10$ kcal./mole

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[6,7]. The molecule BSi_2 was tentatively identified. From the present results, atomization energies of 70 and 250 kcal./mole were derived for BSi and BCSi respectively.

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Heat Capacity of Amorphous Polymers at Low Temperatures

RECENTLY, Starkweather[1] has shown that the model for the heat capacity of chain crystalline polymers proposed by Stockmayer and Hecht[2] can be very useful in understanding thermal motions of polymers at low temperatures. The model assumes that groups in the chain vibrate as units and that there are strong primary bonds between the units and weak interactions between adjacent chains. The temperature dependence of the heat capacity, C_v, can be expressed in terms of two ratios, $C_v/3Nk$ and T/T_m, where N is the number of vibrating groups per gm., T_m equals $h\nu_m/k$, where h and k are Planck and Boltzmann

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