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Carbon: A New View of Its High-Temperature Behavior

Abstract. *An increasing body of research indicates that carbon can exist in a number of polymorphic "carbyne" forms. It is proposed that these forms occur because of a shift to triple bonding in the carbon system as temperature increases above 2600 K. It is also proposed that graphite can dissociate into triple-bonded molecules by a simple mechanism.*

The discovery of new carbon forms in 1968 by El Goresy and Donnay (*1*) and Sladkov and Koudrayatsev (*2*) opened a field of research that is revealing heretofore unsuspected aspects of the behavior of carbon at high temperature. The work of Kasatochkin *et al.* (*3*), the laser Raman results of Nakamizo and Kammereck (*4*), and the work of Fryer (*5*) indicate that these carbon forms contain $-C\equiv C-$ units, probably as chains. Since acetylene is an organic molecule stable at high temperatures, it is reasonable to expect high-temperature carbon forms of this general structure. Also, from a structural point of view, diamond represents the tetrahedral form of carbon and graphite the ring form, and lonsdaleite can be considered a hybrid of these structures. However, before 1968 a polymorph representing triple-bonded carbon was not recognized. Evidently, the new forms fill this gap. The Russian scientists call these new forms "carbynes" (*2*); in this report their nomenclature will be retained.

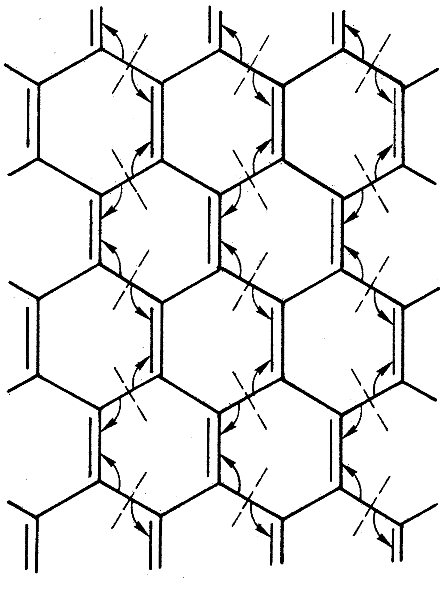

Fig. 1. Mechanism for transformation of a graphite basal plane sheet of atoms into $(-C\equiv C-)_n$ chains.

If the structure of graphite is considered, it is easy to see that it can readily dissociate into $-C\equiv C-$ chains. A mechanism for this is illustrated in Fig. 1, where a portion of a basal plane sheet of atoms from the graphite structure is shown. At high temperatures, a single bond can break and shift an electron into each of the adjacent double bonds. This induces another single bond to break, such that one electron goes to the adjacent "free radical" double bond to form a triple bond and the other goes to the next adjacent double bond. If the process is repeated, as shown in Fig. 1, the entire sheet of atoms separates into $-C\equiv C-$ chains. When it does so, only electrons are shifted to rearrange bonds. Initially, the atoms move only the small distance associated with the change from double to triple bonds. As the new bonds are formed, the bond angles change to produce the linear arrangement of atoms required for $-C\equiv C-$ bonding. This process would be analogous to the well-known high-temperature transformation of benzene to acetylene. The chains can be stacked in a hexagonal array, as proposed by the Russian scientists (*2*), to produce the carbyne forms. Because the chains can be stacked in a number of ways relative to the triple bond positions, one would expect a family of carbyne forms to exist. This indeed appears to be the case. Diffraction data obtained thus far at the Aerospace Corporation indicate that there are eight forms and that there may be more. Kasatochkin *et al.* (*6*) have reported five forms that are in very good agreement with our results. It may be that the carbyne forms are showing what could be called "linear polytypism." Although they appear to be very similar crystallographically, they show a wide range of physical properties. Some forms are very soft, whereas others are superhard—indeed, harder than cubic BN (*7*). This indicates that there must be considerable cross-bonding between chains in some cases. However, the wide range in properties requires a wide variation of the degree of cross-bonding among the various carbyne forms. If cross-bonding between chains is carried to its limit, the result is likely to be the diamond structure. This suggests that these forms may be intermediates in the graphite-diamond transition, and there is a small amount of data in the literature that are consistent with this mechanism (*8*, *9*).

It has been known for several years that the rate of transformation of graphite to a carbyne form (probably chaoite) is very slow compared with that of the reverse transformation. Recently, preliminary rate data have been obtained, and the ratio of the rates was found to be about 500:1, which is consistent with the mechanism proposed in Fig. 1 (*10*). The transformation from the carbyne form to graphite involves a reaction between acetylene-like molecules, which are known to react rapidly and exothermically, whereas the reverse reaction involves the breaking of single bonds as a first step and would be expected to be a much slower process.

The phase diagram in present use must be in error because it does not include the carbyne forms. It has been known for many years that it was difficult to reconcile the high-pressure results with the

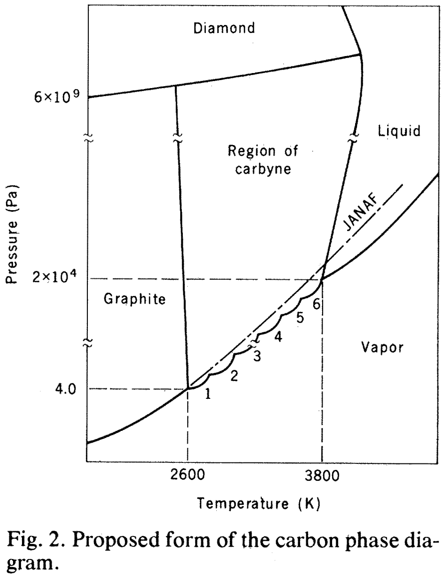

Fig. 2. Proposed form of the carbon phase diagram.

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low-pressure data on the vapor pressure of solid carbon. This difficulty can be removed if a region of carbyne forms is introduced. Because of the number, structural similarity, and unfavorable kinetics of formation of the carbyne forms, it is very difficult to study the phase behavior of carbon at high temperatures. However, after 8 years of effort, new carbon phase diagrams that include the carbyne forms are evolving; the current version is shown in Fig. 2 (*11*). Although this diagram is largely hypothetical, some of its features have been experimentally determined. Its important features are the following.

1) Graphite is not stable above 2600 K at any pressure.

2) The solid-liquid-vapor triple point occurs at 3800 K and 2×10^4 Pa.

3) Carbyne forms are stable between 2600 and 3800 K, and their stability region extends to the diamond transition line.

Along the solid-vapor boundary, the stability range of a particular carbyne form appears to be ~ 200 K; thus about six forms are expected to exist over the total range, as shown in Fig. 2. The remaining forms, therefore, must constitute the higher-pressure forms. Although it is easy to show that carbyne forms exist above 2600 K, it is very difficult to identify the equilibrium species corresponding to the various stability ranges. Consequently, future analysis may establish that the correct number is more or less than six. The transition temperatures of the first three forms are fairly well established at 2600, 2800, and 3050 K; however, except for form 1, which has been tentatively identified as chaoite, their identity is not known. The curve labeled JANAF gives the vapor pressure graphite would have if it were the stable form above 2600 K. Sladkov and Koudrayatsev (*2*) showed that the carbyne forms are stable; therefore, their vapor pressures must lie below the JANAF line. Our results indicate that the equilibrium carbon form that melts to give liquid carbon is probably β carbyne (form 6 in Fig. 2), and that the liquid is transparent, colorless, and of low emissivity (< 0.02). These are the properties that would be expected for a $(-C\equiv C-)_n$ liquid and for the kind of liquid that would be expected to be in equilibrium with a $(-C\equiv C-)_m$ solid.

That carbon shifts to a triple-bonded system whenever possible at high temperatures is also evidenced by the C_3 emission from the gas. It is well known that the C_3 Swing's bands can be observed in emission from carbon gas at 2800 to 3200 K (*12*). However, at temperatures $\geqq$ 3500 K, no Swing's bands appear; this observation is supported by the results of Null and Lozier (*13*) and Howe (*14*). Mass spectrographic studies at temperatures up to 3300 K by Milne *et al.* (*15*) have shown that the C_3 concentration in carbon gas is increasing as expected. Therefore, the C_3 molecule must be shifting to another configuration that has different energy states. Swing's bands come from the double-bonded C_3 molecule, $C = C = C$ (*16*). As the temperature rises, it is conceivable that the configuration of the C_3 molecule could change to the triple-bonded resonance structures: $C\equiv C - C \rightleftharpoons C - C\equiv C$. This could correspond to a state slightly above the $C = C = C$ ground state. Such a shift would account for the disappearance of the Swing's bands at high temperatures, even though the C_3 concentration in the gas increases with temperature. Spectra taken during laser-heating studies indicated a weak band head at 274.2 nm. This is close to a band head at 272.3 nm for acetylene and could result from emission from the triple-bonded form of C_3. It is interesting to note that the molecules with an even number of carbon atoms, such as C_2 and C_4, cannot switch to a resonating triple-bonded configuration. Therefore, the intensity of the C_2 Swan bands should increase with temperature. This is what was observed up to ~ 4500 K. In this respect, it would be interesting to follow C_4 and C_5 emission intensities as a function of temperature.

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7. Hard carbyne forms were produced by quenching carbon gas on a copper substrate in an argon atmosphere at 13.3 Pa. The material was finely crystalline. It was placed on a polished slab of hot-pressed cubic BN and rubbed against the BN surface with a slab of sapphire. The BN was washed and examined with a low-power microscope (40×). Many scratches on the BN surface were easily visible. Electron diffraction patterns obtained from the crystalline material showed it to be a mixture of chaoite and carbon VIII ($a_0 = 9.12$ Å).
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11. A detailed account of the experiments on which the proposed diagram is based will be published elsewhere (A. G. Whittaker, in preparation). The following is a summary of the pertinent observations. The low-temperature stability limit was established many ways, but the high-temperature x-ray studies (*10*) gave the most direct result. At 2590 K, no transformation was detected; at 2680 K, a transformation was easily observed. High-temperature gradient studies gave several transition temperatures. The sample used in this work was a pyrolytic graphite bar measuring 10 by 40 by 1 mm, cut so that the 10 by 40 side was the *a*-face and the 1 by 40 side was the *c*-face. The bar was heated by passing a direct current through a center region ~ 3 mm wide. This produced a temperature gradient of ~ 330 K/mm from the center to the edge. The bar was held at a maximum temperature of ~ 3150 K for ~ 3 minutes. While it was hot its temperature profile was taken with a recording pyrometer. The heating was done in a current of argon at a pressure of 1 atm. The gas flow swept oxygen out of the system and helped cool the bar rapidly when the heating current was stopped. Examination of the bar revealed several bands of differing reflectivity extending the length of the heated portion. Electron diffraction showed the bands to be carbyne forms. The band boundaries could be located on the temperature profile to get the transition temperatures. The values obtained were within ±25 K of those shown in Fig. 2. An approximate temperature limit at high pressure is set by Hall's work on synthetic carbonado [H. T. Hall, *Science* **169**, 868 (1970)]. At ~ 6.5×10^9 Pa and 2500 K, a steel-gray material was produced from natural diamond. Analysis of similar material by electron diffraction gave no diamond or graphite patterns, but showed a mixture of carbyne forms with carbon VI ($a_0 = 9.2$ Å) predominating. The density of the carbynes is greater than that of graphite; therefore the graphite-carbyne boundary slopes, as shown in Fig. 2. Hence, finding carbynes at 2500 K at high pressure is to be expected. Also, this result makes it fairly certain that the graphite-carbyne boundary extends to the diamond transition line. Electron diffraction studies of the deposits on the high-temperature gradient samples and the material obtained by quenching carbon gas and analysis of carbon samples obtained in laser heating experiments show that carbynes are produced over the temperature range 2600 to 3800 K. These results clearly show that the carbon form that melts is a carbyne form. That β carbyne is the form that melts is shown mainly by two observations. Carbon heated to 3800 K and quenched (~ 30,000 K/sec) gave diffraction patterns of β carbyne; also quenched carbon gas from these samples gave the same patterns. Seven observations support the conclusion that liquid carbon forms at 3800 K, but only the two most compelling will be given here. Only at or above 3800 K are spherules and spatters of carbon thrown from a laser-heated spinning carbon rod. That the spatters formed from liquid is self-evident. The detailed structure of the spherules indicated that they were produced from a liquid rather than by condensation of a vapor. High-speed movies showed liquid globs leaving the spinning rod. Occasionally, the liquid would separate from the rod as an irregular sheet. These sheets could be seen to coalesce into spheres under the forces of surface tension. Also, the movies showed that the liquid sheets were very transparent. Attempts to measure the temperature of the liquid by photometric methods showed that at 5890 Å the emissivity of the liquid was <0.02. A transparent liquid would be expected to have a very low emissivity.

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