X-Ray Diffraction Studies of a Graphitized Carbon

CHANGES IN INTERLAYER SPACING AND BINDING ENERGY WITH TEMPERATURE

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This work was undertaken primarily to determine the effect of different atmospheres on the change in the unit cell dimensions of graphite with temperature. The thermal expansion of artificial samples exposed to the following atmospheres and temperatures was determined by standard x-ray techniques and found to be independent of the atmosphere: Nitrogen from −196° to 1016° C., argon from 27° to 1118° C., oxygen from 27° to 474° C., and carbon dioxide from 27° to 896° C. The change of interlayer spacing for this artificial graphite from −196° to 1118° C. is shown to be virtually linear with temperature. The magnitudes of the interlayer spacing at −196° and 1118° C. are 3.339 and 3.465 A., respectively. The coefficient of thermal expansion of the artificial graphite in the direction perpendicular to the basal planes is then 28.6×10^{-6} over this temperature range. Using the experimental values for the interplanar spacing, the interlayer binding energy of graphite is calculated to decrease from 4.0 kcal. per mole at 15° C. to 3.6 kcal. per mole at 1118° C. These results indicate that over the temperature range investigated the atmospheres studied penetrate the graphite lattice only slightly if at all. A comparison of the interplanar binding energy with the energy with which a carbon atom is held in a layer by three covalent bonds indicates the relative insignificance that changes in interlayer binding should have on carbon gasification rates.

THIS investigation was undertaken primarily to determine the effect of different atmospheres on the change in the unit cell dimensions of a graphitized carbon with temperature. The information is of direct interest to gasification studies as an aid in the clarification of such questions as whether or not oxygen penetrates between the graphite layer planes during gasification. Boersch and Meyer (5) have studied by means of electron diffraction the behavior of a graphite filament at temperatures up to 950° C. in oxygen at 10^{-2} mm. of mercury pressure and postulated that the expansion of the lattice along the c axis (an increase in the interlayer spacing) is due to the dissolution of oxygen between the planes. On the other hand, other investigators (12, 17) suggest that gasification of carbon probably occurs along the edges and down through the top basal plane in graphite.

A second phase of the investigation consisted of comparing the coefficient of thermal expansion of a graphitized carbon in different atmospheres with that found in vacuo. Since graphite is a highly anisotropic material, thermal expansion measurements made by the usual dilatometer technique have little meaning, and the wide variety of values reported by those using this method can easily be explained as due to the variation in the degree of orientation produced in the fabrication of their samples. Nelson and Riley (13) recognized this difficulty and made high precision measurements of the thermal expansion of Ceylon graphite in vacuo by means of x-ray diffraction techniques where the diffraction peaks are a function of the direction in a crystal as indicated by Miller indexes.

APPARATUS

In the present investigation, both a 90° (2θ) Norelco and a 180° General Electric spectrometer were used to determine diffraction maxima. For most of the work the Norelco spectrometer, for which a high temperature furnace was available, was used. For the determination of the absolute interplanar spacing of the carbon at room temperature, a General Electric unit, with better resolution, was used. A Gieger counter mounted on a goniometer scanned the spectra over selected angles at the rate of $1/2$° per minute (2θ), and intensity was plotted by a recording Brown potentiometer so that 4 inches of chart paper were equivalent to 1°. Repeated runs were found to reproduce better than ±0.005°. The diffraction peaks were measured at the mid-point of the half-height width.

A high temperature furnace, Figure 1, modeled after one designed by Van Valkenburg and McMurdie (19) as modified by Roy, Middlesworth, and Hummel (16) was adapted to an atmosphere furnace. The furnace itself consists of a platinum ribbon wound refractory tube with two windows positioned 120° from each other to allow passage of the x-ray beam. The protected Chromel-Alumel couple, with junction located $1/4$ inch from the middle of the sample insert, was calibrated with potassium sulfate, which undergoes an inversion at 583° C., and found to reproducibly record the sample temperature within ±5° C.

The sample holder and furnace are surrounded by a gastight chamber having nickel foil windows lined up with the windows of the furnace to permit passage of the x-ray beam. The desired gaseous atmosphere was introduced through a $1/8$-inch ceramic tube located adjacent to the sample holder and was discharged through the two extra holes provided in the ceramic power-inlet tube.

A complete description of the graphitized carbon and of the gases used in the investigation is adequately covered in the preceding paper (20).

EXPERIMENTAL PROCEDURE

The graphitized carbon was ground in an agate mortar and pestle to pass through a 325-mesh screen (U. S. Sieve Series) wetted with a trace of water, and about 0.2 gram was placed in the specimen holder by means of a spatula. After the furnace was assembled, the selected atmosphere was passed through the apparatus at a flow rate of 200 cc. per minute for at least an hour to flush out all air. With the gas flowing, the x-ray pattern from 5° to 85° was obtained at room temperature and then at successively higher temperatures. As the furnace had

a relatively low heat capacity, the time required to raise the furnace temperature in increments of about 150° C. and attain thermal equilibrium was less than 0.5 hour. Preliminary runs showed that change in the unit cell dimension parallel to the layer planes was very small and for all practical purposes could be neglected in the present investigation. On the other hand, expansion perpendicular to the layer planes was large and easily measured by the shift in the 00l x-ray diffraction peaks. For most of the work the 004 peak of the carbon, produced with copper radiation, was used to determine changes in interlayer spacing; but for the carbon dioxide atmosphere, iron radiation was used because of the burning out of the copper tube.
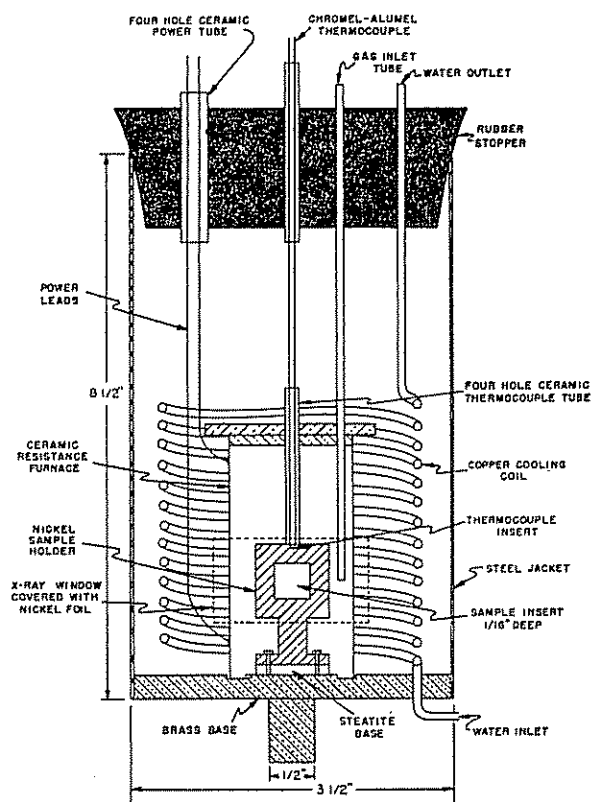

Figure 1. High Temperature X-Ray Diffraction Atmosphere Furnace

For the studies made in a nitrogen atmosphere at −196° C., liquid nitrogen of a purity greater than 99.5% was allowed to boil into the atmosphere furnace. The furnace was rapidly cooled to the point where a layer of liquid nitrogen accumulated on the brass base and kept the sample at a constant temperature. In turn the nitrogen evaporation from the base prevented infiltration of air.

From the x-ray patterns obtained at different temperatures and in different atmospheres, the change in interlayer spacing could be precisely determined. However, because of adsorption and general geometric spectrometer errors, these spacings could not be considered as absolute. In order that all the spacings could be placed on an absolute basis, the interplanar spacing of the graphitized carbon was determined at 30° C., using an internal standard technique similar to that suggested by Bacon (2). High purity sodium chloride was intimately mixed with a sample of the car-

bon, and the sodium chloride angles and corresponding d-values were determined experimentally for the 111, 200, 220, and 222 peaks. These experimental d-values were then compared with those calculated from the known sodium chloride lattice constant of 2.8213 A. at 30° C.—calculated from the spacing of 2.8200 A. at 18° C. (11) and the coefficient of expansion of 4.02×10^{-5} (11)—and a plot was made of the error in d-spacing versus Bragg angle over the range 27.4° to 56.6°. The experimental d-spacings of the carbon determined from the 002 and 004 diffraction peaks were then corrected using this correlation to give the absolute d-spacings. Two independent runs were made using this technique; and interplanar spacings at 30° C. of 3.3608, 3.3619, 3.3612, and 3.3620 A. (average 3.3615 A.) were found using both the 002 and 004 diffraction peaks.

RESULTS

Variation of Interlayer Spacing of Graphite with Temperature. Figure 2 shows the change in the two-dimensional 004 lattice reflections of graphite with changes in temperature in a nitrogen atmosphere. The changes in peak angle are typical of those obtained for the other gaseous atmospheres studied. However, the change in peak intensity of the x-ray beam with change in temperature is affected not only by the increasing amplitude of vibration of the atoms in the solid structure but also by changes in the absorptivity of the atmosphere with temperature. The absorptivity of x-rays by gases at constant pressure decreases with increasing temperature and, hence, causes an increase in the peak intensities. On the other hand, the intensity of the x-ray beam produced by the solid structure decreases with increase in temperature. When the sample was immersed in gases of relatively low absorptivity, such as nitrogen, oxygen, and carbon dioxide, the resulting intensities of the x-ray reflections decreased with increasing temperature. However, when the sample was immersed in argon, the absorptivity of the gas for both the copper and iron radiation was so great that the resulting intensity increased sharply with increase in temperature. The noticeable decrease in intensity of the 004 peak at −196° C. in the nitrogen atmosphere, as shown in Figure 2, was due chiefly to formation of ice on the outside of the nickel foil windows.

Data relating to interlayer spacings for the graphite exposed to various gaseous atmospheres at various temperatures are shown in Table I and Figure 3. These values are based on the previously determined absolute spacing at 30° C. at 3.3615 A. The
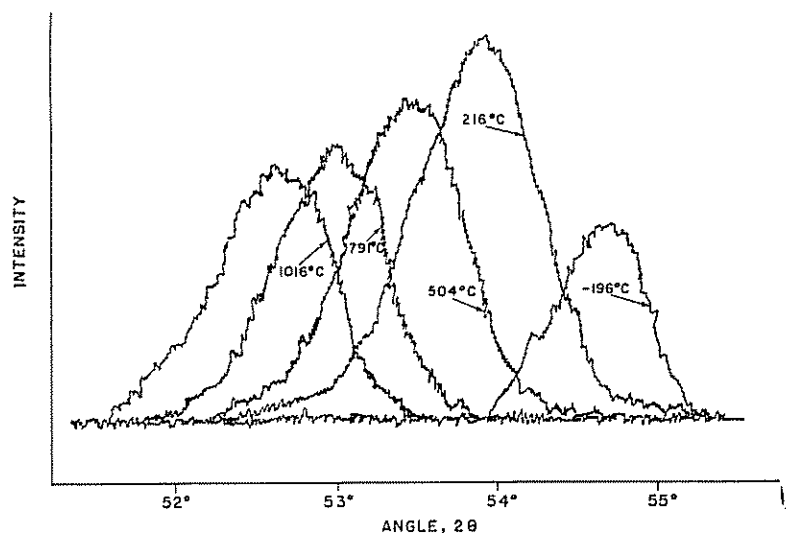

Figure 2. Effect of Temperature on Location of 004 Peaks for a Graphitized Carbon in a Nitrogen Atmosphere

Table I. X-Ray Diffraction Angles for 002 or 004 Peaks in Graphitized Carbon and Corresponding Interplanar Spacings

Temp., °C.	Bragg 004 Angle	Interplanar Spacing, A.	
		Experimental	Equation 1
N₂ Atmosphere, Cu K-alpha Radiation			
—196	27.50	3.339	3.340
28	27.30	3.361	3.361
216	27.15	3.379	3.379
389	27.00	3.396	3.395
504	26.90	3.408	3.406
605	26.84	3.415	3.416
702	26.76	3.425	3.425
791	26.69	3.433	3.434
896	26.61	3.443	3.444
1016	26.50	3.456	3.455
A Atmosphere, Cu K-alpha Radiation			
27	27.30	3.361	3.361
217	27.16	3.378	3.379
525	26.91	3.407	3.408
612	26.83	3.416	3.417
692	26.77	3.424	3.424
783	26.67	3.436	3.433
883	26.63	3.441	3.442
994	26.55	3.450	3.453
1118	26.43	3.465	3.465
O₂ Atmosphere, Cu K-alpha Radiation			
164	27.18	3.375	3.374
314	27.06	3.389	3.388
474	26.95	3.402	3.403
CO₂ Atmosphere, Fe K-alpha Radiation			
	Bragg 002 Angle		
215	16.64	3.380	3.379
416	16.55	3.398	3.398
596	16.47	3.414	3.415
728	16.40	3.428	3.428
896	16.33	3.443	3.444

data were evaluated by linear regression, and it was shown that the probability of the interlayer spacing being within ±0.0004 A. of that reported in Table I is 95%, which is somewhat lower than the possible error in c which was estimated from errors in measurement of the diffraction angles and temperature. Considering the low accuracy with which the fourth decimal place is known, the spacings reported in Table I have been rounded off to the third decimal place. For the oxygen and carbon dioxide atmospheres there was, of course, a slow reaction at the maximum temperature: but as the x-ray patterns were determined in less than 0.5 hour after reaching these temperatures, the amount of sample reacted could be considered as negligible.

As shown in Figure 3, the variation of the interplanar spacing with temperature is virtually linear. Use of a least squares equation involving t^2 to describe the trend was considered, but the t^2 term would place the accuracy of the equation above experimental accuracy; hence, a linear equation, determined by least squares, was used. The equation has the form

$$c = 3.358_6 + 9.52 \times 10^{-5} t \qquad (1)$$

where c is in Angstrom units and t is in °C. A comparison between the experimental points and those calculated by the equation is included in Table I.

Equation 1 gives an interplanar spacing of 3.360 A. at 15° C. This spacing, according to the work of Franklin (10) and Bacon (3, 4), suggests a structure intermediate between fully crystalline graphite with a spacing of 3.354 A. at 15° C. and completely nongraphitic carbon with a spacing of 3.44 A. at 15° C. Using the equation suggested by Bacon relating interplanar spacing to the proportion (p) of disoriented layers, the sample would appear to contain approximately 20% nongraphitic structure. It perhaps should be pointed out, however, that recent results of Ruston (8), where he reports interplanar spacings of 3.34 A. for some charcoals, throws some doubt on the validity of using the interplanar spacing to determine the proportion of disoriented carbon.

The coefficient of expansion of the graphitized carbon, perpen-

dicular to the layer planes, from —196° to 1118° C., based on the spacing at 15° C., is calculated to be 28.6 × 10⁻⁶. Although there is an appreciable change in the c spacing of graphite with temperature, no change in the a spacing, obtained from the 100-line, could be detected. This, of course, is the result of the strong covalent bonding of carbon atoms within the lattice planes as compared to the very much weaker bonding between planes.

Changes in Interlayer Binding Energy of Artificial Graphite with Temperature. Calculation of the change in the interlayer binding energy of fully crystalline graphite with temperature has been made possible by the recent work of Brennan (6), who developed energy equations for the attractive and repulsive forces between the layer planes. These equations were based on the assumption that the interlayer binding results from van der Waals forces, each layer being treated as a molecule. The equations for the attractive and repulsive energies have the form

$$E_A = \frac{n\pi\sigma A}{x^4} \sum_{s=1}^{\infty} 1/s^3 \qquad (2)$$

and

$$E_R = 24.918 n e^{(-0.78269x - 0.01794x^2)} \qquad (3)$$

where

E_A and E_R = attractive and repulsive energies, respectively, in units of $e^2/2a_0 = 13.60$ ev.
n = number of cells in a layer
σ = surface density of atoms in units of the first Bohr radius, $a_0 = 0.5292$ A.
A = variable, determined so that the minimum of the total energy curve occurs at the known equilibrium separation of the layers in the crystal
x = interlayer distance

It is important to appreciate that the only factors that vary with temperature in Equation 2 are x and A. However, Equation 3 was derived from the results of quantum mechanical calculations based on the ratio, Z^*/n^*, where Z^* is the screening constant and n^* is the quantum number of the electrons at the respective temperature. The crux of the calculation then is the as-
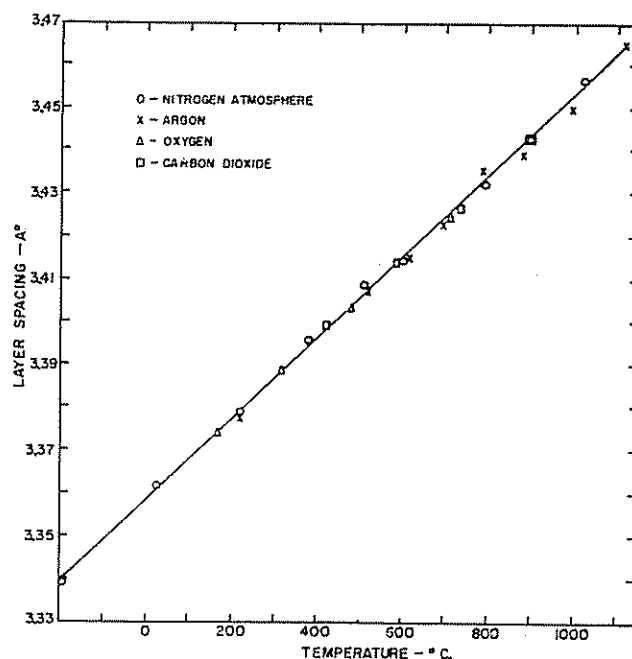
Figure 3. Variation of Interplanar Spacing of a Graphitized Carbon with Temperature

sumption that both Z^* and n^* are constants essentially independent of temperature. Certainly a maximum temperature of 1118° C. is not sufficient to cause a quantum jump and, hence, n^* can safely be considered independent of temperature in the present investigation. According to Brennan (7), Z^* should be determined by the in-plane binding, and even though over the temperature range investigated the bond distances must change slightly, the effect must be small compared to the interplanar changes. Therefore, the energy equations have been used in the form presented for all temperatures. The solution involves setting the differential of the total energy equation ($E = E_A + E_R$) equal to zero when x has its equilibrium value at a given temperature, solving for A, and using this value to calculate the binding energy. Since the unit cell contains two atoms, the energy per mole contributed to the graphite crystal by the interlayer binding is then $U = (1/4) [N_A(E/n)]$, where N_A is the Avogadro number. Table II presents the pertinent values for the calculation of the binding energy of graphitized carbon at 15° C. and at a maximum temperature, 1118° C. At temperatures between 15° and 1118° C., the binding energies will take intermediate values.

Table II. Variation of Interlayer Binding Energy of Graphitized Carbon with Temperature

Temp., °C.	x, A.	A	Kcal./Mole U_A	U_R	U
15	3.360	544	−10.6	6.6	−4.0
1118	3.465	523	−9.0	5.4	−3.6

Gasification of Graphitized Carbon by Carbon Dioxide or Oxygen. The x-ray patterns of graphitized carbon were followed during reaction with oxygen at 474° C. and with carbon dioxide at 896° C. The nickel sample holder held approximately 0.2 gram of the carbon, which permitted reaction for several hours at these temperatures before consumption of the sample. Although somewhat inconclusive, it is believed that the results should be mentioned. The main point of interest was whether or not the oxygen or carbon dioxide molecules penetrated between the layer planes during reaction. If such penetration occurred, an increase of the interplanar distance would be expected, such as has been reported (15) with graphitic oxide. This increase in planar spacing would then shift the 002 and 004 peaks to smaller angles. During the entire reaction cycle with both oxygen and carbon dioxide, the x-ray band was scanned carefully for even the slightest trace of such new peaks and none detected. Work on the detection of trace crystal arrangements in a solid has been done, using the present machine and the detection of 10% of one structure in another is readily accomplished. The conclusion may be drawn, therefore, that if oxygen or carbon dioxide penetrated between the crystallite planes during reaction, it did so to an extent of less than 10% of the sample.

Another point of interest on which it was hoped some information could be obtained was the preferential reaction of certain crystallite sizes in graphitized carbon. For example, Foresti (9) reported that a reacted graphitized carbon had a larger average crystallite size than an unreacted sample. In the present investigation, the shapes of the 002 and 004 peaks were followed very closely during reaction and were observed to increase in half width. Other conditions remaining constant, this would indicate a decrease in the average crystallite size with reaction. However, the selection of this reason for the widening of the peak width is unwarranted at present since it was observed that there was some unevenness in reaction along the sample. This produced a sample of uneven depth which would distort the diffracted beam and produce a wider peak width. Studies along this line would have particular merit if a rod sample was used and corrections applied to the change in sample diameter.

DISCUSSION OF RESULTS

In obtaining the data reported in Table I, the samples were ground to −325 mesh. Thus, the maximum particle size may have been upwards to 100 times larger than the average crystallite dimension. There is, therefore, some question as to whether all crystallite faces were actually exposed to the gaseous atmosphere employed. Within this limitation, however, the results show that the atmosphere to which the carbon is exposed has no measurable influence upon interplanar spacing over the temperature range investigated.

The variation of interplanar spacing with changes in temperature found for the graphitized carbon can be compared to the data for Ceylon graphite reported by Nelson and Riley (13). Over the temperature range, 15° to 800° C., the latter report the variation as $c = 3.3525 + 90.54 \times 10^{-6}t + 6.33 \times 10^{-9}t^2$, where c is in Angstroms. The values of the c spacing at 15° C. and 800° C., as given by this equation, are 3.3539 and 3.4290 A., or an increase in interplanar spacing of 0.0751 A. From Equation 1, the spacings of the artificial graphite used in this investigation at 15° C. and 800° C. are 3.3600 and 3.4348 A., or an increase in interplanar spacing of 0.0748 A. It is thus seen that the magnitude of the change in interplanar spacing with temperature of the two carbons is quite close even though the absolute values of the spacing are somewhat different. Using the p correlation of Bacon and Franklin, the Ceylon graphite of Nelson and Riley is seen to be completely graphitic ($p = 0$) in comparison to a $p = 0.20$ for the artificial graphite. However, since the increase in interplanar spacing of the two graphites is in good agreement it would indicate that the so-called nongraphitic fraction has a coefficient of expansion very close to that of graphitic carbon.

In further comparison to the work of the authors, Nelson and Riley outgassed their 300-mesh (British Standard Sieve Series) Ceylon graphite at 850° C. prior to determining its expansion in vacuo. However, again the close agreement between the two sets of data leads to the belief that either the adsorbed gases do not affect the spacing or that they were not sufficiently removed at 850° C. There is reason to believe that the latter is true since workers (1, 14) show that adsorbed nitrogen, oxygen, and hydrogen on carbon are removed chiefly at temperatures between 1500° and 2000° C. under vacuum.

The equations of Brennan, based on van der Waals attraction between planes, give 4 kcal. per mole for the binding energy of "molecular" planes as compared to the 20 kcal. per mole postulated by Ruff (17). The authors feel that the values determined from Brennan's equations are more in line with the following evidence:

1. As shown by Brennan, this energy for the interlayer binding produces a predicted volume compressibility for graphite that is very close to that found experimentally by Bridgeman (8).
2. Simple extrapolation of the known carbon-carbon bonding energies versus carbon-carbon bond distances leads to a predicted interlayer binding energy of only a few kcal. per mole. Even though this approximation is rough, it at least is thought to be of the correct order of magnitude.

It is appreciated that the Brennan equations are based on fully crystalline graphite. However, the close agreement between the change in interlayer spacing of fully crystalline Ceylon graphite and of the artificial graphite indicates a negligible difference in binding energies for unoriented and oriented planes. If this were not true, the significantly different binding energies of the two species would be expected to make a detectable difference in the magnitude of expansion. Moreover, Brennan calculated the interlayer binding energy for the radical case where all layers have the same orientation (one atom lying directly over another) and found an energy change of only 0.36 kcal. per mole. In the present case, with a much less radical change in structure, the difference would be expected to be less. Therefore, the differ-

ence in binding energies for unoriented and oriented planes would be less than the difference in mean binding energy for the artificial graphite between 15° and 1118° C. of 0.40 kcal. per mole, and nan's equations can be applied in the simple manner described.

As suggested by Brennan, graphite may be considered an idealized molecular crystal with each layer plane an independent molecule. Expansion studies by Nelson and Riley and the authors bear this out by showing insignificant interaction between the in-plane bonds in each molecule and the bonding between planes. That is, an appreciable change in the bonding distance between molecules showed, at best, a minute change in the in-plane bond distances. This is reasonable if one compares the strength of the in-plane bonds of approximately 40 kcal. per mole (meaning that each carbon atom in the plane is held with a combined energy amounting to 120 kcal. per mole) with the much lower bonding energy between molecules. Therefore, even though the interplanar bonding energy between the molecular graphite planes shows a substantial decrease of 13% in going from room temperature to 1118° C., such a decrease would not be expected to significantly affect the ease of pulling a carbon atom from a molecular plane (or the gasification rate), since this should chiefly be determined by in-plane bonding.

The x-ray examination of graphitized carbon during reaction with oxygen and carbon dioxide, within the limitations of the experimental technique, bears out the belief that the reacting gases do not penetrate the crystal lattice. It must be recognized, however, that the graphitized carbon is composed of an agglomerate of minute crystallites and that all faces of all these crystallites may not be oriented in such manner as to permit contact between reactant gas and planar crystallite edges. If, as might be possible, considerable orientation of crystallites occurs during graphitization, it is conceivable that penetration of the reactant might be prevented by unfavorable orientation rather than ent inability to do so under the conditions investigated. Certainly a more direct investigation of the possibility of oxygen penetration during reaction would be the use of a single graphite

crystal. Here the reacting gas would have access to all the interplanar spaces of the solid and the presence or absence of interplanar penetration could be more accurately determined and related to the reaction mechanism. The results obtained here, however, should be indicative of the reaction mechanism possible for artificial graphites and carbons of the type investigated.

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Adsorption-Desorption Studies of Nitrogen, Argon, and Carbon Dioxide on Carbon Rods

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LOW temperature gas adsorption is a convenient technique for obtaining information of the surface area and pore structure of solids. However, when the areas determined by this technique are related to the gasification or combustion properties of carbon at high temperature, a question arises as to whether or not the area available to a gas molecule at low temperatures is in any way comparable to the area available to the same molecule at elevated temperatures. The answer to this question would be expected to depend primarily upon the pore structure of the carbon under investigation, with carbons containing numerous pore strictions likely to show the greatest effect of temperature on the availability of their area.

Recent work on the surface areas of coal and coal chars indicates that these solids act like molecular sieves. Maggs and

Bond (12), for example, find that the internal structure of bituminous coal chars can be pictured as a collection of large pores connected to the surface by molecular size capillaries. They find that over 55% of the area of some chars lies beyond pore constrictions 5.7 A. or less in diameter. Malherbe (13, 14) finds that B.E.T. surface areas determined for South African coals are a function of the adsorbate used. If room temperature adsorbates such as methanol or water are used, the surface areas are as much as 30 times higher than areas determined for low temperature argon adsorption. This difference is attributed to the swelling of the coal by the methanol or water with the resulting penetration of these molecules into previously unavailable molecular capillaries. Lecky, Hall, and Anderson (10) recently compared the adsorption of water and methanol vapors on American