# AMORPHOUS CARBON AND GRAPHITE

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GEOMETRICAL factors play an important rôle in the molecular architecture of solids : molecules, atoms and ions all possess definite size and shape ; homopolar valency bonds are directed in space and it is therefore difficult to conceive how a solid, particularly one in which homopolar bonds play a major part, can have a completely random crystal structure. The examination by X-ray diffraction methods of substances which show no obvious crystalline characteristics and previously were considered amorphous, e.g., vitreous and highly dispersed solids, animal and vegetable fibres, soaps, etc., has shown that the great majority possess structural characteristics which are typical of the crystalline state. As a result of the X-ray examination of a number of specimens, P. Debye and P. Scherrer [1] concluded that amorphous carbon is merely graphite in a state of sub-division, so fine that it could never be reached by mechanical means. P. P. von Weimarn and T. Hagiwara [2] maintained, from experiments on the precipitation of barium sulphate, that even when X-ray diffraction photographs indicate that a substance is amorphous, this must not be taken as a proof that it is so.

Glassy or vitreous solids make up an important group of the so-called amorphous substances. A comparison of X-ray powder photographs of silica, wollastonite, sodium diborate, selenium, potash and soda felspars, boric oxide, complex silicates, glucose and sucrose, in the vitreous and the crystalline state, led J. T. Randall, H. P. Rooksby, and B. S. Cooper [3] to put forward the " crystallite " theory of the vitreous state. They showed, for example, that the main features of the diffraction pattern of vitreous silica can be accounted for by the assumption that it consists of exceedingly minute crystals of crystobalite, with average linear dimensions of the order of 15 A., and lattice constants some $6 \cdot 6\%$ greater than those of large crystobalite crystals. W. H. Zachariasen [4] pointed out that this suggestion leads to discrepancies between the observed and the calculated densities and is not in accord with the characteristic mechanical and thermal properties of the glasses : he suggested that the ultimate condition for the formation of a glass is that the substance can form an extended three-dimensional network of atoms, lacking periodicity, with an energy content comparable with that of the corresponding crystal network. G. Hägg [5] put forward what is perhaps a compromise between the above views, namely, that the formation of a glass is due to the presence of large or irregular groups of atoms, too cumbersome for direct addition to the lattice. M. L. Huggins, Kuan-Han Sun, and A. Silverman [6] have pointed out that a solid will readily assume the

[1] *Physikal. Z.*, 1917, **8**, 291.

[2] *Kolloid-Z.*, 1926, **38**, 129 ; *Kolloidchem. Beih.*, 1927, **23**, 400.

[3] *Z. Krist.*, 1930, **75**, 196.      [4] *J. Amer. Chem. Soc.*, 1932, **54**, 3841.

[5] *J. Chem. Physics*, 1935, **3**, 42.      [6] *J. Amer. Ceram. Soc.*, 1943, **26**, 393.

amorphous state if the regular network structure (crystalline) has practically the same energy content as the irregular : in certain glasses, besides homopolar valency bonds, hydrogen bonds also probably have an important function in building up the irregular network.

In an attempt to show how far our knowledge of the structure of the so-called " amorphous " carbons is compatible with the above views, we shall first of all consider the crystal structure of graphite, then the crystal chemistry of amorphous carbon and of its transition into graphite, and finally discuss its relationship with other amorphous substances. Throughout we shall use the term " amorphous carbon " in its usual sense, viz., for those forms of black carbon, other than macro-crystalline graphite, which possess no obvious crystalline characteristics.

*The Graphite Lattice.*—The graphite crystal structure which first received wide acceptance was that deduced by J. D. Bernal[7] and by O. Hassel and H. Mark[8] a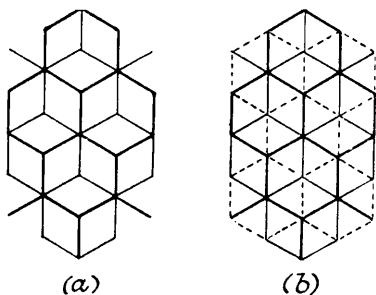nd later confirmed by C. Mauguin[9] and H. Ott :[10] it consists of carbon atoms arranged in flat, honeycomb-like layers which are stacked parallel to and equidistant from each other in such a way that half the atoms in one layer lie normally above half the atoms in the layer beneath, while the other half are normally above the centres of the hexagons of the layer beneath : alternate layers lie, atom for atom, normally above each other. The C–C spacing in the layers is 1·42 A., whilst adjacent layer-planes are 3·35 A. apart.[11] D. S. Laidler and A. Taylor,[12] however, pointed out that this structure does not account for the presence of certain faint lines in the X-ray powder photographs of both natural and artificial graphites : these lines had previously been reported by G. I. Finch and H. Wilman[13] in electron-diffraction photographs of graphite. To explain the presence and intensity of these additional diffractions, H. Lipson and A. R. Stokes[14] suggested that many graphites have a composite structure made up of about 80% of the ordinary (Bernal) structure, 6% of a disordered structure (turbostratic) and 14% of the structure originally suggested by Debye and Scherrer (*loc. cit.*) : in this structure the flat honeycomb planes are stacked parallel to each other as in the Bernal structure, but instead of alternate layers being normally above each other the layers follow an *abcabc* sequence, the third layer being symmetrically related to the planes above and below (see Fig. 1, *a* and *b*). These two ways of stacking hexagon layer-planes are reminiscent of the manner in which close-packed planes of spheres can be



(a)    (b)

Fig. 1

[7] *Proc. Roy. Soc.*, 1924, *A*, **106**, 749.    [8] *Z. Physik*, 1924, **25**, 317.
[9] *Bull. Soc. franç. Min.*, 1926, **49**, 32.    [10] *Ann. Physik*, 1928, **85**, 81.
[11] J. B. Nelson and D. P. Riley, *Proc. Physical Soc.*, 1945, **57**, 477.
[12] *Nature*, 1940, **146**, 130.    [13] *Proc. Roy. Soc.*, 1936, *A*, **155**, 345.
[14] *Ibid.*, 1942, *A*, **181**, 101.

stacked to give either the close-packed hexagonal or the face-centred cubic structure according to whether the stackings follow the *ababab* or the *abcabc* sequence respectively. The phenomenon may have some connection with the metallic character of the inter-planar valency bonding in graphite. The lattice structure of graphite, however, is not yet fully elucidated : J. Gibson [15] has recently obtained powder photographs of ash-free graphites, both natural and artificial, which show some 16 faint lines which cannot be indexed on the basis of either of the two structures described above.

In addition to the crystallographic there is also physical and chemical evidence in support of the layer-lattice structure of graphite. Its pronounced electrical, magnetic, and mechanical anisotropy is in keeping with this structure : so also are the close parallelism between the chemical properties of graphite and those of the triarylmethyls,[16] and the lamellar reactions of graphite.[17]

*Amorphous Carbon.*—Certain types of amorphous carbon show crystochemical reactions similar to those of macrocrystalline graphite ; *e.g.*, O. Ruff and O. Bretschneider [18] state that norit, an active carbon, freed from oxygen and water vapour by ignition, reacts with elementary fluorine at 280° to form a solid monofluoride containing 57·3% of fluorine [theory for $(CF)_n$, 61·27%], which they suggest has fluorine atoms intercalated between hexagon layer-planes of carbon atoms as in the compound made from macrocrystalline graphite.

U. Hofmann and A. Frenzel [19] have shown that certain apparently amorphous carbons give good yields of graphite oxide when oxidised with potassium chlorate in the presence of concentrated sulphuric and nitric acids (see Table I). Sugar charcoal, however, when treated similarly was

TABLE I

*Composition and Yield of Graphite Oxide*

| Carbon used. | Percentage composition. | | | Percentage yield of graphite oxide calculated on carbon present. |
|---|---|---|---|---|
| | C. | $H_2O$. | C : O. | |
| Ceylon graphite . . . . . . | 55·8 | 13·9 | 2·45 | 95·6 |
| Acheson graphite . . . . . . | 55·7 | 11·7 | 2·28 | 92·3 |
| Carbon monoxide carbon . . . | 53·4 | 10·8 | 1·99 | 83·3 |
| Retort carbon . . . . . . | 53·3 | 11·5 | 2·02 | 87·6 |
| Petroleum soot . . . . . . | 52·3 | 13·2 | 2·02 | 20·2 |

oxidised practically completely to gaseous and soluble colloidal products, no graphite oxide being formed. This reaction has been used as a means of

[15] *Nature*, 1946, **158**, 752.

[16] H. L. Riley, *J. Inst. Fuel*, 1937, **10**, 149.

[17] Detailed summaries of the lamellar reactions and compounds of graphite have been given by W. Rüdorff, *Wien. Chem. Ztg.*, 1944, **47**, 172, and H. L. Riley, *Fuel*, 1945, **24**, 1.

[18] *Z. anorg. Chem.*, 1930, **217**, 1.          [19] *Ber.*, 1930, B, **63**, 1248.

differentiating amorphous from graphitic carbon. M. Berthelot in 1870 defined graphite as "toute variété de carbon susceptible de fournir par oxydation un oxyde graphitique." W. A. Selvig and W. C. Ratliff [20] used the Brodie reaction (oxidation with fuming nitric acid and potassium chlorate) to determine the proportion of graphitic carbon in coals and cokes, and from their results concluded that the former contain no graphitic carbon, whilst the latter contain only a small amount ($< 1\%$). Hofmann and Frenzel (*loc. cit.*), on the basis of their $X$-ray results (see below), however, argue that these differences in graphite oxide yield are due to differences in crystallite size and packing rather than to any fundamental difference in the crystal structures of graphitic and amorphous carbons : the much smaller crystallites of the chars and cokes are more readily oxidised to soluble products than the larger crystallites in graphitic carbons. It is significant, however, and we shall return to this point again, that the amorphous carbons which give relatively large yields of graphite oxide are those made by deposition from the gas phase.

K. Fredenhagen and G. Cadenbach [21] found that potassium, rubidium, and cæsium react, not only with macro-crystalline graphite, but also with soot, pure arc carbon, wood charcoal, and active carbon ; whereas sodium reacts with soot, but not with graphite. From more detailed investigations on the interaction of potassium and a soot, made by the incomplete combustion of a tar oil, K. Fredenhagen and H. Suck [22] concluded that under the same conditions graphite and soot take up practically the same amount of potassium : the establishment of equilibrium with the soot required much longer than with the graphite ; the pretreatment of the soot played some part in determining the velocity of the absorption and desorption of the potassium. These results and those of the $X$-ray study of $(C_8K)_n$ and $(C_{16}K)_n$ by A. Schleede and M. Wellmann [23] suggest that lamellar structures are present in soot.

The intercalation of bromine between the layer-planes of the graphite crystal lattice has been investigated by W. Rüdorff,[24] who found that graphites take up about $80\%$ of their weight of bromine, whatever their state of subdivision : active carbon takes up about $170\%$ of its weight of bromine, probably because of its more highly developed crystallite surface.

H. H. Lowry and S. P. Morgan [25] prepared graphite in a highly dispersed state by first oxidising it to graphite oxide and then subjecting the product to thermal decomposition and repeating this treatment on the resulting graphite : the final product possessed from one-third to one-quarter of the adsorptive power of the best active charcoal. E. Berl, K. Andress, L. Reinhardt, and W. Herbert [26] concluded from $X$-ray and electrical conductivity measurements that there is no truly amorphous carbon in active carbons : its properties differ from those of graphite because of the size and mesomorphous character of its crystallites ; the electrical conductivity of samples

[20] *J. Physical Chem.*, 1925, **29**, 1105.
[22] *Ibid.*, 1929, **178**, 353.
[24] *Z. anorg. Chem.*, 1941, **245**, 383.
[26] *Z. physikal. Chem.*, 1932, **158**, 273.

[21] *Z. anorg. Chem.*, 1926, **158**, 249.
[23] *Z. physikal. Chem.*, 1932, *B*, **18**, 1.
[25] *J. Physical Chem.*, 1925, **29**, 1105.

prepared at high temperatures may approach that of macrocrystalline graphite.

The above properties of amorphous carbon are qualitatively in keeping with the Debye–Scherrer hypothesis that they consist of exceedingly minute graphite crystallites. There are, however, amorphous carbons which possess properties which this hypothesis cannot explain.

Cokes and chars always contain an appreciable proportion of chemically combined foreign matter ; e.g., carbonisation of carbohydrates up to 1000° gives chars containing 1—2% of combined oxygen which is not eliminated by prolonged heating in a vacuum at the same or a lower temperature ; only prolonged heating at much higher temperatures eliminates this oxygen. That it plays an important rôle in the structure of amorphous carbon is indicated by studies of nitrogenous and sulphurous carbons. Amorphous carbon does not take up nitrogen when strongly heated in the gas ; if, however, it is heated in gaseous ammonia, hydrogen cyanide is formed and the carbonaceous residue may contain up to 3% of nitrogen.[27] E. Terres [28] studied the carbonisation of nitrogenous organic compounds such as glycine, asparagine, etc., and obtained nitrogenous cokes. W. Hook [29] and H. E. Blayden, J. Gibson, and H. L. Riley [30] have contrasted the analysis of chars prepared at various temperatures from carbohydrates on the one hand, and from glycine on the other : it is significant that the former, even those prepared at 1000°, all contain appreciable quantities of oxygen ; the latter all contain nitrogen, but oxygen is present only in the chars prepared at the lower temperatures. The 1200° glycine char contains 3·64% of nitrogen but no oxygen. Sulphurous chars have been prepared by heating sucrose char with elementary sulphur,[31] by carbonising organo-sulphur compounds [32] and by heating semi-coke, filter-paper, and wood in a current of sulphur dioxide.[33] The sulphur in these products cannot be removed by exhaustive extraction with sulphur solvents and in some cases amounts to several per cent. In addition to oxygen, nitrogen, or sulphur, cokes and chars, even when prepared at high temperatures, always contain appreciable amounts of hydrogen. These foreign atoms all probably play an important part in disordering the atomic arrangement in amorphous carbons.

The X-ray powder photographs of amorphous carbons are strikingly different from those of macrocrystalline graphites : not only are the diffractions much broader but they are also fewer in number, most specimens giving only two or three highly diffuse haloes, instead of the numerous sharp diffractions in the graphite X-ray photograph. A much deeper insight into the crystallographic character of amorphous carbon has been obtained from

[27] W. G. Mixter, *Amer. J. Sci.*, 1893, **45**, 363.

[28] *J. Gasbeleucht.*, 1916, **59**, 519.

[29] *Carnegie Schol. Mem. Iron and Steel Inst.*, 1936, **25**, 81.

[30] " The Ultra-Fine Structure of Coals and Cokes," *B.C.U.R.A.*, London, 1944, 176—231.

[31] J. P. Wibaut, *Rec. Trav. chim.*, 1919, **38**, 159 ; *Proc. K. Akad. Wetensch. Amsterdam*, 1921, **24**, 92.

[32] R. Ciusa, *Gazzetta*, 1922, **52**, 130 ; 1925, **55**, 385.

[33] F. Fischer and A. Pranschke, *Brennstoff-Chem.*, 1928, **9**, 361.

the detailed study of these $X$-ray powder photographs. The diffracting units are of colloidal dimensions and therefore, because of their low resolving power, give diffuse diffractions : there is a quantitative relation between this diffuseness and the size of the diffracting unit. The first explanation of the disappearance of all the $hkl$ diffractions and most of the high-order diffractions in the powder photographs of amorphous carbons was put forward by Berl, Andress, Reinhardt, and Herbert [26] and by H. Arnfelt : [34] it is briefly as follows. In these finely crystalline or so-called amorphous carbons, the hexagon layer-planes are stacked parallel to each other in the individual crystallites, with a spacing approximately equal to, or somewhat greater than, the corresponding spacing in the graphite crystal ; the individual hexagon layer-planes, however, are otherwise orientated in a completely random manner. J. Biscoe and B. E. Warren [35] have coined the word *turbostratic* to describe such a crystallographic structure. It can give rise to only $00l$ and $hk0$ (more correctly $hk$) diffractions : the $hk$ bands are cross-lattice diffractions formed by the individual hexagon layer-planes acting as two-dimensional diffraction gratings. Such diffractions are not symmetrical but show " tails " towards greater values of $\theta$.

B. E. Warren [36] has discussed in detail this type of diffraction and derived a formula relating the broadening of the cross-lattice band with the linear dimension of the diffracting net-plane ; this is of the same form as the Scherrer formula for three-dimensional crystallites but the numerical constant, instead of being approximately unity, is 1·84 :

$$\text{Linear dimension of crystallite, } L = \frac{1 \cdot 84 \lambda}{\beta \cos \theta}$$

where $\lambda$ is the wave-length of the $X$-radiation, $\beta$ the breadth of the diffraction at half its peak intensity (half-peak width), and $\theta$ the Bragg angle. Warren has also shown that with very small crystallites there is a small displacement of the diffraction maximum of the cross-lattice band towards a larger value of $\theta$

$$\Delta(\sin \theta) = \frac{0 \cdot 16 \lambda}{L}$$

If a correction is not made for this displacement, the calculated C–C spacing within the hexagon layer-planes will be too small.[37]

The assessment of the average size and shape of the crystallites present in amorphous carbons from the broadening of the diffraction bands in $X$-ray powder photographs has been attempted by several workers. Unfortunately, different methods of calculation have been employed, particularly in correcting the measured half-peak width for the width of a diffraction from a similar specimen made up of large crystals : the results reported by different workers, therefore, are often not strictly comparable. Nevertheless, the results reported for similar carbons are of the same order of magnitude. Because

[34] *Ark. Mat. Ast. Fys.*, 1932, **23B**, No. 2.

[35] *J. Appl. Physics*, 1941, **9**, 492.   [36] *Physical Rev.*, 1942, **49**, 693.

[37] Cf., for example, H. E. Blayden, H. L. Riley, and A. Taylor, *J. Amer. Chem. Soc.*, 1940, **62**, 180 ; J. H. de Boer, *Rec. Trav. chim.*, 1940, **59**, 826 ; U. Hofmann, *Naturwiss.*, 1944, 260.

usually only two diffraction bands are of sufficient intensity for accurate measurement, it has become customary to express the results of measurements of this kind in terms of a hypothetical, average, cylindrical crystallite, the diameter, $L_a$, of which is termed the $a$ dimension, and the height, $L_c$, the $c$ dimension. Some typical results [38] are shown in Table II. These, and the results of other workers, indicate that the original Debye–Scherrer theory of the crystallographic nature of amorphous carbon requires modification in at least two respects, viz., the small crystallites in amorphous carbon differ from macro-crystalline graphite in that (1) they are turbostratic, and

TABLE II

*Crystallite Dimensions* (Hofmann and Wilm [38])

| Carbon. | Analysis %. | | | Layer-plane spacing, $c/2$, A. | Crystallite dimension, A. | |
|---|---|---|---|---|---|---|
| | C. | H. | Ash. | | $L_a$. | $L_c$. |
| Ceylon graphite . . . . . | 99·1 | 0·0 | 0·3 | 3·35 | ∞ | *ca.* 200 |
| Carbon monoxide carbon 700° . | 94·9 | 0·1 | 4 | 3·4 | 120 | 180 |
| ,, ,, ,, 550° . | 95·0 | 0·1 | 3 | 3·4 | 150 | 160 |
| ,, ,, ,, 420° . | 91·8 | 0·1 | 2 | 3·4 | 60 | 70 |
| ,, ,, ,, 400° . | — | — | — | 3·45 | 40 | 35 |
| Acetylene soot (explosive decomposition) . . . . . . . | 99·7 | 0·3 | 0·0 | 3·43 | 45 | 50 |
| Retort carbon . . . . . . | 96·9 | 0·3 | 0·6 | 3·45 | 45 | 40 |
| Acetylene soot . . . . . . | 95·0 | 0·8 | 0·3 | 3·55 | 21 | 13 |
| ,, ,, calcined . . . | 99·1 | 0·3 | 0·3 | 3·55 | 26 | 14 |
| ,, ,, activated . . . | 98·5 | 0·0 | 0·5 | 3·6 | 22 | 16 |
| Active carbon AKT IV . . . | 88·5 | 1·7 | 1·1 | 3·5 | 17 | 11 |
| ,, ,, ,, calcined . | 96·5 | 0·35 | 1·1 | 3·45 | 25 | 10 |
| ,, ,, ,, activated | 94·4 | 0·0 | 2·0 | 3·65 | 18 | 8 |
| Supranorit . . . . . . . | 89·3 | 0·6 | 0·3 | 3·5 | 18 | 8 |
| ,, calcined . . . . | 97·3 | 0·15 | 0·4 | 3·45 | 26 | 7 |
| ,, recalcined 30 hrs. . . | — | — | — | 3·55 | 26 | 7 |
| ,, activated . . . . | 97·7 | 0·0 | 0·9 | 3·7 | 24 | 7 |
| Carboraffin calcined . . . . | 96·2 | 0·6 | 1·8 | 3·6 | 23 | 10 |
| ,, activated . . . . | 93·0 | 0·0 | 3·3 | 3·7 | 19 | 7 |
| Gas-mask carbon calcined . . | 97·4 | 0·6 | 0·5 | 3·55 | 20 | 10 |
| ,, ,, activated . . | 96·5 | 0·0 | 1·0 | 3·6 | 17 | 8 |
| Sugar carbon . . . . . . | 98·1 | 0·7 | 0·0 | 3·6 | 21 | 9 |
| ,, ,, activated . . . | 98·0 | 0·0 | 0·0 | 3·6 | 18 | 7 |

(2) the hexagon-layer spacing is not constant at 3·35 A., but increases as the number of layer-planes in the crystallite decreases. Even when allowance is made for the uncertainty in the fundamental accuracy [39] of these results, the extreme minuteness of these crystallites is striking : in the smaller crystallites the individual hexagon layer-planes are not much larger than certain polynuclear aromatic molecules of known structure and the $c$ dimensions indicate that the crystallites can be built up from as few as three or four layer-planes.

[38] U. Hofmann and D. Wilm, *Z. Elektrochem.*, 1936, **42,** 504.

[39] G. H. Cameron and A. L. Patterson, *Amer. Soc. Testing Mat.*, Symposium on Radiography and X-ray Diffraction, 1937.

It would appear from the above that the process of charring or carbonisation must involve the progressive transformation of the more or less complex organic matter into the polynuclear aromatic ring systems and their subsequent stacking and growth. Some such process is indicated by the experiments of R. C. Smith and H. C. Howard [40] who charred pure cotton cellulose
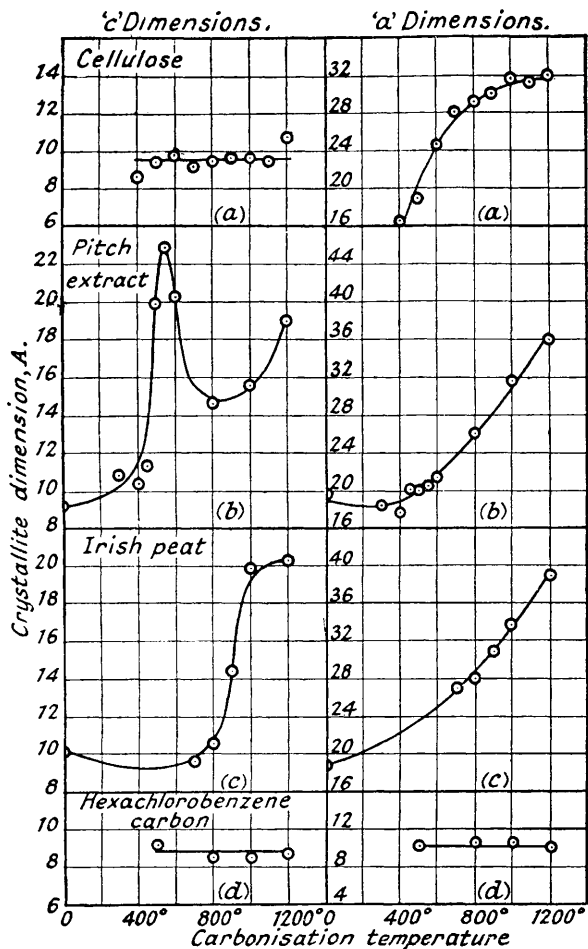


FIG. 2

at temperatures ranging from 190° to 400° and subjected the products to exhaustive oxidation with alkaline permanganate : the magnitude of the yields of aromatic acids from the various chars indicated progressive aromatisation as the charring temperature increased. X-Ray investigations have shown, however, that this simple picture is far from complete. Fig. 2(a) summarises the results of crystallite-size determinations on chars

[40] J. Amer. Chem. Soc., 1937, 59, 234.

prepared from cellulose at various temperatures.[41] Results of an identical character have been reported by U. Hofmann and F. Sinkel [42] who worked with sucrose chars. The striking feature of these results is the constancy of the average height ($c$ dimension) of the crystallites (experimentally, the half-peak width of the 002 diffraction band) over a wide range of carbonising temperature. Crystallites built up merely from polynuclear aromatic layer-planes, held together by relatively weak van der Waals forces, would not be expected to behave in such a manner, but rather to vary their degree of packing with the speed and temperature of carbonisation. This variation would be reflected in changes of the $c$ dimension. Other carbohydrates, lignin, and wood, *i.e.*, organic compounds containing a relatively high proportion of oxygen, all give chars containing crystallites with $c$ dimensions between 9 and 10 A. Carbonising conditions can be varied between wide limits, with respect to both speed and temperature (up to 1200°), without any consequential change in the half-peak width of the 002 diffraction of the resulting char. Cellulose carbonised in an atmosphere of ammonia, and also glycine, behave in a similar manner, but the constant $c$ dimension is somewhat greater, *viz.*, between 12 and 13 A. This constancy of the $c$ dimension is highly suggestive and appears to indicate some kind of cross-linking between the layer planes of the crystallites.

This hypothesis appears more probable when we consider the $X$-ray crystallographic behaviour on carbonisation of certain organic compounds which have a relatively small oxygen content. Fig. 2($b$) shows the $c$-dimension curve obtained with cokes made over a range of temperatures from that part of a bituminous coal-tar pitch which is soluble in carbon tetrachloride. Similar $c$-dimension curves [43] are given by pitches, certain bitumens, bituminous coals, the pyridine–chloroform soluble extracts of bituminous coals and certain pure polynuclear aromatic compounds, *e.g.*, dibenzanthrone, Caledon jade-green, etc. Such $c$-dimension curves appear to be characteristic of the presence in the parent carbonaceous matter of large, thermally stable, lamellar, aromatic molecules. Aromatic hydrocarbons of this type are volatile and apparently the presence of some oxygen and/or nitrogen in the parent molecule is necessary for a large carbon yield : the proportion, however, must not be too large, otherwise charring occurs at a low temperature. These $c$-dimension curves have been interpreted as follows. The ascending part of the curve, between room temperature and about 500°, indicates a unidimensional crystallisation, brought about by the increased packing of thermally stable aromatic molecules under the influence of thermal vibration. The maximum at about 500° reflects the conversion of a system consisting of stable, independent organic molecules, held together by weak dispersion forces (molecular lattice) into a " carbon " crystallite [rigid, three-dimensionally cross-linked(?) lattice]. Dibenzanthrone, after being heated slowly up to 475° and cooled, still gives its characteristic $X$-ray diffraction

[41] H. E. Blayden, H. L. Riley, and A. Taylor, *J.*, 1939, 67.
[42] *Z. anorg. Chem.*, 1940, **245**, 85.
[43] H. E. Blayden, J. Gibson, and H. L. Riley, *J. Inst. Fuel*, 1945, War Time Bulletin, 117.

pattern made up of several more or less sharp diffractions ; after heating to 500° the pattern characteristic of the dibenzanthrone crystal lattice has completely disappeared and been replaced by two diffuse haloes, characteristic of amorphous carbon.   This change, *molecular lattice* → *carbon*, occurs over a relatively narrow range of temperature, the height of which appears to be a function of the proportion of oxygen in the parent carbonaceous material.   Substances like cellulose form rigid (cross-linked ?) carbon crystallites at temperatures little above 200°, whereas certain coking coal bitumens retain their molecular identity up to temperatures as high as 550°.

The interpretation of the descending portion of the *c*-dimension curve between 550° and 900° [Fig. 2(*b*)] is not quite so clear.   The phenomenon is, however, of general occurrence : whenever a carbonaceous substance on being heated to some temperature below 550° gives a product which contains crystallites having an average *c* dimension greater than about 12 A., then a further increase of temperature brings about a decrease in the *c* dimension (experimentally, a broadening of the 002 diffraction).   The increasing disorder over this temperature range may be due to the evolution of oxygen as oxides of carbon, and a consequent reduction in the extent of the cross-linking between the hexagon layer-planes.   The subsequent increase in the *c* dimension above 900° is perhaps facilitated by the remnants of the ordered structure which the system possessed at 550°.

A further type of *c*-dimension curve is shown in Fig. 2(*c*) : it is characterised by an abrupt increase in the average *c* dimension in the temperature range 800—1000°.   Crystallite growth of this kind is shown by peats, to a less extent by brown coals and lignites, and also by " bituminised " cellulose and lignin, *i.e.*, cellulose or lignin which has been heated in an autoclave to about 300° with an excess of aqueous alkali.[43]   In the case of peat, the crystallite growth of a part of the char between 800° and 1000° is so great as to suggest some profound atomic rearrangement, perhaps a kind of polymorphic change.   Although the true nature of this crystallographic change is still not clear, J. Gibson, M. Holohan, and H. L. Riley [44] have pointed out that, besides the diamond and graphite lattices, there is a third possible spatial arrangement of carbon atoms which may play an important part in the atomic architecture of amorphous carbon.   This arrangement can be pictured as follows.   Imagine a graphite layer-plane to be made up of discrete hexagons connected together by valency bonds, as in Fig. 3(*a*) ; break the necessary bonds and rotate the hexagons *A,B,C*, etc., inwards through 60° [Fig. 3(*b*)] ; it will be found that the valencies so freed can be attached without strain to those of similarly tilted hexagons in adjacent planes, above and below.   This can be seen in Fig. 3(*c*), which shows the spatial relationship of 4 hexagons.   The structure so formed is a three-dimensional network of the " skeleton lattice " type, full of large holes and long channels and reminiscent of the structure of certain zeolites.   The disappearance of the flat layer-planes suggests that the resonance energy of this structure would be less than that of the graphite lattice, and its existence therefore less probable.   The new structure, however, contains an orderly

[44] *J.*, 1946, 458.

network of conjugated double linkages running throughout the whole three-dimensional lattice and its resonance energy would therefore be of an appreciable magnitude. The existence of such a structure is made more probable by the discovery by I. L. Karle and L. O. Brockway,[45] by means of electron-diffraction measurements, of the non-co-planarity of o-tetraphenylene [see Fig. 3(c)]. The suggested structure is a three-dimensional repetition of o-tetraphenylene residues.
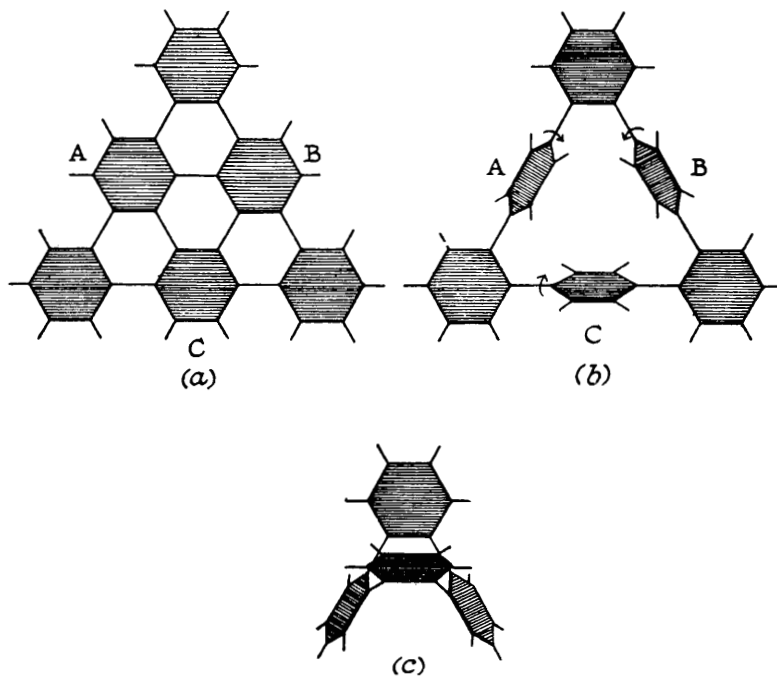


(a)            (b)

(c)

FIG. 3

A consideration of carbonising processes which would possibly tend to give some structure other than the flat, honeycomb network of carbon atoms led Gibson, Holohan, and Riley to prepare carbon by (a) carbonising hexaiodobenzene and (b) the interaction of hexachlorobenzene and sodium amalgam ; (a) gave a carbon which showed practically no coherent scattering of X-rays and (b) gave a carbon, the X-ray powder photograph of which, although highly diffuse, showed new features which can be explained by the existence of small volumes of the three-dimensional network described above. The constancy of both the a and the c dimensions [Fig. 2 (d)] when a carbon prepared by method (b) (temperature of preparation did not exceed 300°) was heated to higher temperatures provides additional evidence of a rigid, cross-linked lattice structure.

These X-ray investigations leave little doubt that the idea that black amorphous carbons are merely graphite in an extremely fine state of sub-

[45] J. Amer. Chem. Soc., 1944, 66, 1974.

division is inadequate and needs further qualification.   It is evident that the structure of a particular sample may be greatly influenced both by the nature of the parent carbonaceous material and by the method of carbonisation.   It is difficult to conceive, for example, how a system consisting of relatively free and independent lamellæ could fail to develop some degree of order under the influence of thermal vibration, and yet carbons can be made which give no coherent scattering of X-rays.

Before outlining a modified view of the crystallographic nature of amorphous carbons, we must consider the process of graphitisation, *i.e.*, the transition, *amorphous carbon → graphite.*

*Graphitisation.*—The high thermal stability of pure amorphous carbon is shown by the results of Biscoe and Warren [35] (Table III) who studied the

TABLE III

*Crystallite Dimensions of Carbon Black* (Biscoe and Warren)

| Time and temp. of heating. | Layer-plane spacing, A. | | Crystallite dimension, A. | |
|---|---|---|---|---|
| | From 002. | From 004. | $L_a$. | $L_c$. |
| — | 3·55 | 3·41 | 20·0 | 12·7 |
| 2 hrs. at 760° | 3·53 | 3·43 | 22·6 | 14·4 |
| 2 hrs. at 1040° | (3·65) | 3·47 | 28·0 | 14·9 |
| 2 hrs. at 1500° | 3·48 | 3·45 | 44·2 | 24·9 |
| 2 hrs. at 2000° | 3·46 | 3·44 | 55·8 | 32·3 |
| 2 hrs. at 2800° | 3·45 | 3·44 | 65·2 | 40·0 |
| 2 hrs. at 2000° | 3·47 | 3·43 | 60·5 | 35·5 |
| 2 hrs. at 1040° | 3·55 | 3·46 | 29·8 | 14·9 |

effect of high temperature on the crystallographic character of a commercial carbon black.   Similar results were obtained by P. Corriez [46] who studied the effect of high temperature on the crystallite dimensions of sucrose chars. In the case of pure carbons it is only at extremely high temperatures that pronounced thermal recrystallisation occurs.   U. Hofmann, A. Ragoss, and F. Sinkel [47] have shown by means of X-ray diffraction, electron-microscope and adsorption studies that the small, polycrystalline, spherical particles of carbon black, on heating for 24 hrs. at 3000° undergo thermal recrystallisation to an extent limited by the size of the original spherical particle, *i.e.*, the individual polycrystalline particles probably become single crystals. This thermal stability of the amorphous carbon crystallites is due, of course, to the high resonance energy of the hexagon network planes of carbon atoms. It is only when these networks are broken down by some chemical mechanism that pronounced crystal growth can occur at temperatures below 2000°. This was realised by E. G. Acheson long before the crystal structure of graphite was known : in his original patent on the manufacture of graphite

[46] *Compt. rend.*, 1935, **201**, 1189.
[47] *Kolloid-Z.*, 1941, **96**, 231 ; see also D. Wilm and U. Hofmann, *ibid.*, 1935, **70**, 21 ;   A. Ragoss, U. Hofmann, and R. Holst, *ibid.*, 1943, **105**, 118 ;   M. von Ardenne and U. Hofmann, *Z. physikal. Chem.*, 1941, *B*, **50**, 1.

he states : [48] " I have also discovered that, in order to produce pure graphite from carbonaceous materials, there is an indirect conversion and that the act of formation of the graphite is more in the nature of an act of dissociation of the carbon from its combination with other materials than a conversion of the ordinary carbon into graphite, and that as a preliminary step, the carbon has to be combined chemically with some other material. Thus I have found that if the carbonaceous material or carbon used in the process contains a considerable proportion of mineral matter or if it is mixed with a certain proportion of oxide or oxides such as silica, clay, alumina, manganese, lime, or oxide of iron and subjected to treatment as hereinafter set forth (high temperature), the yield of graphite is enormously increased and the product is most satisfactory."

It is significant too that processes which involve the formation of carbon by deposition from the gas phase often give, at relatively low temperatures, products which are highly crystalline : see, for example, the crystallite dimensions of the carbons formed on a catalyst by the reaction $2CO = C + CO_2$, quoted in Table II. The growth mechanism of the carbon crystallites formed in such reactions apparently involves the initial formation of single carbon atoms which subsequently attach themselves to pre-formed graphite nuclei. Other reactions are known which give rise to highly crystalline graphite at temperatures far below that of thermal recrystallisation : they all involve the liberation of individual carbon atoms : e.g., the graphitisation of austenite,[49] and the decomposition of carbides [50] and calcium cyanamide.[51] Carbons deposited from hydrocarbon gases, in the neighbourhood of 1000°, are not so highly crystalline as those deposited from carbon monoxide at the same temperature : the presence of hydrogen appears to inhibit crystal growth, presumably by saturating the valencies of the carbon atoms at the surface of the crystallites. It is reasonable to suppose, however, that carbons formed by any process which involves the participation of single carbon atoms will have the most stable structure, i.e., the flat, layer-plane, graphite-like structure, rather than any cross-linked structure of rather higher potential energy. M. Holohan and R. Iley [52] have shown that, in spite of their highly dispersed state, carbon blacks and carbon deposited from the gas phase on vitreous silica at 1000°, have ignition temperatures which approach and may even exceed those of natural and artificial graphites. The $X$-ray-scattering power of carbons of this type is

[48] U.S.P. 568,323, 29.9.1896 : quoted by F. A. J. Fitzgerald, *J. Soc. Chem. Ind.*, 1901, **20**, 443 ; see also H. Ditz, *Chem. Ztg.*, 1904, **28**, 167, and W. C. Arsem, *Met. Chem. Eng.*, 1911, **9**, 536.

[49] F. Wüst and C. Geiger, *Stahl u. Eisen*, 1905, **25**, 1134, 1196 ; K. Iokibe, *Sci. Rep. Tôhoku Imp. Univ.*, 1920, **9**, 275 ; L. Northcott, *J. Iron Steel Inst.*, 1923, **108**, 491.

[50] H. Ishikawa, *Elect. Rev. Japan*, 1931, **19**, 419, 493, 690, 726, 824, 884 ; C. Hahn and A. Strutz, *Metallurgie*, 1906, **3**, 725 ; *Chem. Ztg.*, 1907, **31**, Rep. 33 ; J. Westbecker, *Metallurgie*, 1904, **1**, 137 ; *Z. Elektrochem.*, 1904, **10**, 837 ; A. Frank, *Versamm. Ges. deutschen Naturforscher u. Aerzte*, Sept. 1905 ; *Chem. Ztg.*, 1905, **29**, 1044 ; V. M. Weaver, U.S.P. 1,576,883, 16.3.26.

[51] E. Collett and M. Eckardt, E.P. 5713, 7.3.1911 ; A. Remelé and B. Rassow, *Z. angew. Chem.*, 1920, **33**, 139 ; N. Kameyama, *J. Chem. Ind. Japan*, 1921, **24**, 1131.

[52] Unpublished work of the Northern Coke Research Laboratory.

much greater than that of chars of comparable crystallite size : sulphurous chars (see above) have a still lower scattering power. Although these differences in scattering power have, as yet, only been studied semi-quantitatively, they are of such a magnitude that there is little doubt of their significance.

*Conclusion.*—The above considerations lead to the conclusion that amorphous carbons are built up from two types of structure, *viz.*, (I) the turbostratic lamellar, graphite-like structure and (II) the disordered, three-dimensionally cross-linked structure (Fig. 3).

Amorphous carbons which contain a preponderance of structure I are usually much purer than those made up largely of II : it is possible that the foreign atoms, hydrogen together with oxygen, nitrogen, or sulphur, play some part in stabilising the type II disordered structure.

Such a view of the crystallographic character of amorphous carbon appears to offer a reasonable basis for the explanation of the great diversity of its properties, *e.g.*, the highly specific nature and range of its adsorptive properties, the great variation in its chemical reactivity, the differences in its mechanical properties and scattering power for $X$-rays, etc. Carbons deposited from the gas phase, which may contain little or no combined oxygen, will be made up largely of type-I structures, whilst chars and cokes in general will consist of intimate associations of both types. A large proportion of oxygen in the parent carbonaceous matter appears to favour the formation of structure II, whereas carbonaceous matter containing little oxygen and a large proportion of benzenoid carbon, *e.g.*, pitches, bitumens, etc., will give carbons with a higher proportion of structure I. Both structures possess high thermal stability : structure II appears to persist in some specimens at temperatures well above 1000°.

No mention has been made of the importance of the secondary structure, *i.e.*, the cohesion and degree of agglomeration of the crystallites, in determining the properties of amorphous carbon. Carbon blacks used in the rubber industry have been investigated in detail ; [53] little is definitely known, however, of the secondary structure of chars and cokes : their accessible surface can be measured but the open lattice present in both structures I and II makes the interpretation of such measurements difficult.

Such is the diversity of the crystal structure of solids that no single comprehensive theory of the amorphous state is possible. Metals and salts can be so disordered by mechanical strain or dispersion that they give diffuse $X$-ray diffractions. Crystals which are made up of long homopolar chains exist in an amorphous condition when the chains become tangled together, *e.g.*, vitreous sulphur and selenium, rubber, borate-glass, etc. Systems in which the molecules are large lamellæ can assume the amorphous (or mesomorphous) state because of the difficulty these cumbersome units have in packing into an ordered lattice, *e.g.*, pitches, bitumens, polynuclear aromatic compounds. Finally, there is the disordered three-dimensional network present in certain glasses and vitreous solids. Amorphous carbons should probably be placed in a class intermediate between the disordered lamellæ and the disordered cross-linked lattice.

[53] Columbian Carbon Company, " The Particle Size and Shape of Colloidal Carbon as Revealed by the Electron Microscope," New York, 1940.