11. *Studies in Graphite Formation. Part III. An X-Ray Study of the Carbonisation of* (a) *Cellulose and* (b) *Bituminous Coal.*

By H. E. BLAYDEN, H. L. RILEY, and A. TAYLOR.

The dimensions of the graphite crystallites in cokes prepared under different conditions over the temperature range 400—1300° from (*a*) cellulose and (*b*) coal have been determined from Debye–Scherrer powder photographs. As the temperature increases, the crystallites show a relatively rapid growth along the *a* axis up to 700°, above which the growth is much slower. In each case the *c* dimension remains constant over the range of carbonising temperature studied. The *c* spacing is apparently dependent upon the number of layer planes in the individual crystallites, increasing as this number decreases. An attempt has been made to determine the relationship between the number of unsaturated border atoms of the hexagon planes in the crystallites and the disordered organic matter. The results indicate that when the carbonisation temperature reaches 600—700°, the amount of disordered organic matter is insufficient fully to satisfy the valency requirements of the border carbon atoms. This fact explains the abrupt changes which occur in the properties of cokes prepared at this carbonisation temperature.

THE choice of cellulose as the starting material for these investigations was determined by the following considerations. (*a*) The molecular structure of cellulose is known (Meyer and Mark, *Z. physikal. Chem.*, 1929, *B*, **2**, 115; Cross and Clark, *Z. Krist.*, 1938, **99**, 357). (*b*) It can readily be obtained in a relatively high state of purity in the form of ashless filter-paper. (*c*) It gives reasonably good yields of carbonaceous residue on pyrolysis. (*d*) This pyrolysis has been studied in detail by Smith and Howard (*J. Amer. Chem. Soc.*, 1937, **59**, 234). (*e*) The carbonisation process is essentially one of aromatic condensation (Riley, *Gas World*, 1937, Coking Section, **25**, 118), and a starting material devoid of aromatic structure possesses certain advantages.

The mechanism of the carbonisation process has been pictured by Hofmann (*Ber.*, 1932, *B*, **65**, 1821) as follows: In the initial stages, highly condensed aromatic molecules are formed which arrange themselves in a graphite-like layered structure. As the temperature rises, graphite nuclei are formed surrounded by chemically bound complex hydrocarbon rings and chains. These can neither be extracted by solvents nor removed in high vacuum at 500°, and it is therefore inferred that they are chemically bound round the borders of the hexagon planes of the graphite nuclei. As coking proceeds, they decompose, some of the carbon atoms being lost in the form of volatile compounds, the remainder attaching themselves to the edges of the hexagon planes, so causing the lateral growth of the graphite crystallites.

The above picture is only qualitative, and the object of the present investigation was to make it quantitative, to determine the laws which govern crystallite growth during carbonisation, and if possible, to learn something more of the nature of the disordered carbon, hydrogen, and oxygen atoms present in the cokes.

Samples of carbon were prepared from (*a*) pure cellulose (Whatman's filter paper: ashless, hydrochloric and hydrofluoric acid extracted), (*b*) a Northumberland coal, by carbonising it in nitrogen under precisely controlled conditions to a predetermined temperature. The percentage yield of carbonaceous residue, which was carefully analysed, was determined in each experiment. An *X*-ray powder photograph of the residue was also taken, from which the dimensions of the crystallites were determined.

The broadening of the *X*-ray diffraction lines by crystals smaller than 10^{-5} cm. has been investigated by a number of workers. Scherrer (Zsigmondy, "Kolloidchemie," 3rd Edn., 1920, 387), Seljakow (*Z. Physik*, 1925, **31**, 439), Bragg ("The Crystalline State," Bell & Sons, Ltd., 1933, Vol. 1, 189), and Warren (*Z. Krist.*, 1938, **99**, 448) have derived a formula connecting the diffraction broadening for cubic crystals of cubic form. Von Laue (*ibid.*, 1926, **64**, 115) derived a formula covering the general case of crystals of parallelepipedal form belonging to any crystal system, *i.e.*, of a crystal of edge lengths m_1a_1, m_2a_2, m_3a_3, where the *m*'s are numbers and the vectors *a* define the unit cell.

When orthorhombic or hexagonal crystals referred to orthohexagonal axes are considered von Laue's formula simplifies to

$$\beta = C\lambda/\varepsilon \cos \tfrac{1}{2}\chi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\varepsilon = \sqrt{\Sigma(h_i/a_i)^2/\Sigma(h_i/m_ia_i^2)^2}$, β is the pure diffraction broadening from a point specimen, λ is the wave-length of the *X*-radiation, $\frac{1}{2}\chi = \theta$, the Bragg angle at which the maximum falls, and $h_i = h_1$, h_2, or h_3, the indices of reflexion. When the h_100, $0h_20$, $00h_3$ reflexions in turn are considered, (1) simplifies further to

$$\beta = C\lambda/m_ia_i \cos \tfrac{1}{2}\chi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

from which we can compute directly m_ia_i, the crystallite dimension in the direction of a_i.

This equation is of exactly the same form as that obtained by Scherrer for crystals of cubic form and cubic symmetry. The investigators differ as to the value of *C*, which has been quoted as 0·94 (Scherrer), 0·92 (Seljakow), 0·89 (Bragg), and 0·94 or 0·89 by Warren, according to the method of calculation. Von Laue gives the values 0·5 or 0·92, but after correction of errors in his calculation, the possible values become 1·0 or 1·46. Jones (*Proc. Roy. Soc.*, 1938, *A*, **166**, 16) has recalculated the value of $C = 1{\cdot}0$, a value which is used in this paper.

The determination of β presents some difficulty. The experimental conditions are such that the size of the focal spot, the position of the camera with respect to the target, the size of the cylindrical Debye–Scherrer camera, the radius of the specimen and its absorptive factor for *X*-rays, the dimensions of the slit system, and the characteristics of the film and the microphotometer used all play their parts in determining the shape of the observed spectrum lines. Cameron and Patterson (American Society for Testing Materials, Symposium on Radiography and *X*-Ray Diffraction, 1937) and Randall ("The Diffraction of *X*-Rays and Electrons by Amorphous Solids, Liquids and Gases," Chapman and Hall, Ltd., 1934) review the efforts made by different workers to overcome these difficulties.

Scherrer (*loc. cit.*) considered the case of a finite cylindrical specimen of diameter *b*, situated at the centre of a cylindrical Debye–Scherrer camera, irradiated by a monochromatic, parallel beam of *X*-rays. He obtained the observed breadth *B* by measuring directly across the photometer curve of the spectrum line at a position of half the maximum intensity. The diffraction broadening is then given by

$$\beta = B - b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and b is considered constant at all angles. Haley and Terrey (*Trans. Faraday Soc.*, 1936, **32**, 1313) showed that in certain cases this assumption could give negative values for the particle sizes of colloidal gold. They then used Brill's first modification of von Laue's theory (Randall, Rooksby, and Cooper, *Z. Krist.*, 1930, **79**, 196), correcting the experimentally observed line widths by calculation.

Jones (*loc. cit.*) has adopted a mixture method which enables the particle-size determinations to be made by using a standard cylindrical camera with a reasonable slit system and specimen. The method adopted is as follows. A suitable powder consisting of large particles, considered infinitely big, is mixed with the substance to be investigated. The Debye–Scherrer photograph then reveals the sharp lines from the large crystallites and the diffuse bands from the material under investigation. Both sets of lines have in this manner been obtained under exactly the same conditions. From the set of sharp lines it is possible to interpolate the widths b of lines produced by infinitely large particles at the position of the peaks of the diffuse lines. Jones then develops a graphical method of determining from the observed widths B of the diffuse lines their true diffraction broadening β. For this purpose, a curve connecting the ratios β/B and b/B is plotted by making various assumptions as to the nature of the diffraction broadening and the observed shape of the unbroadened lines. From the experimental data, b/B is readily found, and hence β, the true diffraction broadening.

Von Laue defines the line width as $\beta = \int I(\chi)\mathrm{d}\chi/I(\text{max.})$, where I is the intensity of the line at the angle χ. The line shape is influenced by a number of factors, among which the particle-size distribution must play an important part. The larger particles sharpen the peak, and the smaller ones broaden the line base. The Scherrer definition (see above) of line breadth tends to favour the large particles, and the Laue definition is to be regarded as giving a truer mean size. Using von Laue's definition of line width, Jones points out that if the Scherrer correction formula $\beta = B - b$ is used, the errors will be small enough to be neglected in regions where β/B tends to unity (small crystallite sizes) but considerable when b/B tends to unity.

The mixture method can only be used in special cases. It is particularly suitable when the sharp lines of the standardising substance are clear from the diffuse lines produced by the crystallites under investigation. Favourable cases are thus most likely to be found among cubic crystals where the intervals between the lines are fairly regular and where the lattice parameter is small. Perhaps the most favourable case is that of copper–gold alloys (Jones and Sykes, *Proc. Roy. Soc.*, 1938, *A*, **166**, 376). Here we have a set of superlattice lines of variable breadths spaced regularly between the sharp reflexions produced by the principal lattice. As the regions of order grow, so do the superlattice lines decrease in width, and the growth and extent of the nuclei where order exists can be computed.

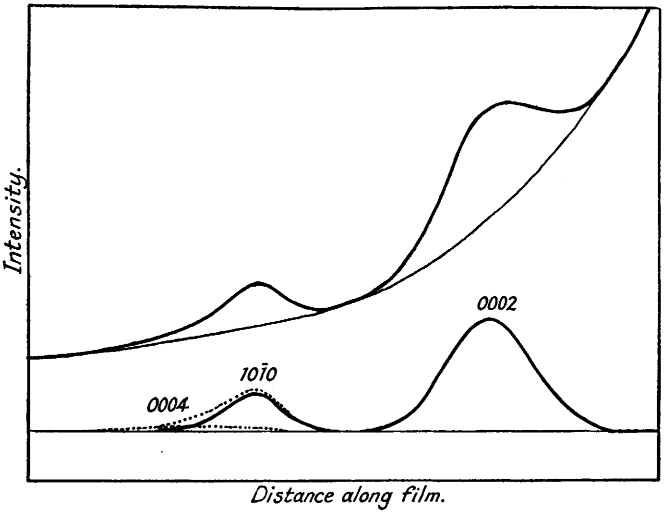
" Amorphous carbons " and graphites do not present so favourable a case. The crystal symmetry is hexagonal and the lines fall in awkward positions, so that it is very difficult to use the mixture method. However, a compromise has been reached, where, by carefully standardising the conditions, the best features of Jones's method have been realised. Instead of interpolating to determine the value of b for an unbroadened line at the positions of the maximum of one of the diffuse bands from small crystallite carbon, it has been possible to *measure this value directly*, because the peaks from macrocrystalline carbon (considered as of infinite size) fall almost exactly in the positions of the band maximum from the so-called " amorphous carbons "; b was measured for each sharp line in turn, and formula (3) used to obtain β, the true diffraction broadening for the bands which fell in the same place. Thus, variations in b (not assumed to be constant) were automatically eliminated, and fairly accurate values of β in the regions for $\beta/B \approx 1$ were thus obtained.

The photographs from which the particle sizes were computed were all taken in a 9·0-cm. diameter standard Debye–Scherrer powder camera of the Bradley type, cobalt-K_α radiation from a Metro-Vickers X-ray tube being used. All specimens were made from carbons sieved through wire gauze (350 meshes to the linear inch). The sieved material was mixed with a small amount of very dilute glue solution. A thick-walled glass capillary tube of ½ mm. bore was filled with the damp powder, which was then compressed and pushed out of the tube as a cylindrical rod about 1 cm. long. The rod was carefully dried in an oven at about 80° for 10 minutes, and accurately centred in the camera. The very small crystallites present made it unnecessary to rotate the specimen, the slightest wobble with its consequent line broadening thus being prevented.

All the photographs were taken under exactly the same conditions, and because of the very low absorption coefficient of carbon for cobalt-K_α radiation, the variation from specimen to specimen was insignificant. It was therefore possible to use a specimen of pure graphite as the standardising material.

A number of very pure graphites were photographed in a large camera, 19 cm. in diameter, and a sample selected which gave a very sharp resolution in the high-order reflexions. Jones (*loc. cit.*) points out that for the large crystallites a large camera and long wave-length are to be preferred. A photograph of the same graphite specimen was then taken in the 9-cm. camera, and the line widths computed by the Laue method described above. As far as possible the exposure times and development were controlled so that the intensities of the lines were on the linear portion of the film density–*X*-ray intensity curve. Calibration steps were photographed on all films so that any deviation from linearity could be corrected. The films were carefully microphotometered by means of a manual instrument of our own construction at intervals of 0·2 mm. (0·1 mm. in the special case of the pure large crystalline graphite). The readings so obtained were plotted on a large scale, 2·0 cm. of graph corresponding to 1 mm. of film. The curves were redrawn on to a flat background, and from these the values of *B* for the various lines were computed by the Laue method.

FIG. 1.



The value of *b* from the sharp lines was found to be the same for the 0002 and the $10\bar{1}0$ reflexions. These were the only reflexions of immediate concern for the very small crystallites under investigation. It was found that only the 0002, 0004, $10\bar{1}0$, and $11\bar{2}0$ reflexions were present. In all cases the $11\bar{2}0$ reflexion was too weak to be of use in the crystallite size determination. The $10\bar{1}1$ reflexion which normally lies adjacent to the $10\bar{1}0$ was absent. This can be explained by the irregular arrangement of the net planes relative to each other. Each net plane therefore contributes independently to the $10\bar{1}0$ reflexion, which can be considered as a cross grating line. This is in accord with the ideas of Lowry and Bozorth (*J. Physical Chem.*, 1928, **32**, 1524), Arnfelt (*Arkiv Mat. Astr. Fys.*, 1932, **23**, *B*, 1), and Berl, Andress, Reinhardt, and Herbert (*Z. physikal. Chem.*, 1932, *A*, **158**, 273), and of Hofmann and Wilm (*Z. Elektrochem.*, 1936, **42**, 504) for graphitic oxide and various carbons of small crystalline dimensions.

The 0004 reflexion contributes to the "tail" of the broadened $10\bar{1}0$ line. To separate these lines in order to get a value of *B* for the $10\bar{1}0$ reflexion, the exact position and intensity of the 0004 reflexion were computed, and the line width of the 0004 adjusted to give the same crystallite size as the 0002. The computed 0004 line was then subtracted from the original photometer contour to give the true line shape of the $10\bar{1}0$ reflexion (see Fig. 1). The indices

TABLE I.

Analyses, Crystallite Dimensions, and Parameters of Cokes Prepared from Cellulose at 200—1300°.

Carbonising rate, 5°/min.; radius of camera, 45·1 mm.; radius of specimen, 0·25 mm.; half peak width, *b*, 0002 and 10$\bar{1}$0, 1·25 mm.; radiation : Co-K_α.

Final carbn. temp.	Analyses, %.*			Yield, % (dry basis).	Lattice parameter, A.		C–C dist. $=\frac{a}{\sqrt{3}}$, A.	Inter-layer-plane dist. $=c/2$, A.	*a* Axis.		*c* Axis.		Crystallite dimensions, A.	
	C.	H.	O (diff.).		*a* axis.	*c* axis.			Line width, *B*, mm.	$1/\beta$.	Line width, *B*, mm.	$1/\beta$.	*a* axis.	*c* axis.
200°	44·01	6·29	49·73	98·93	—	—	—	—	—	—	—	—	—	—
400	78·45	4·06	17·49	32·62	—	—	—	—	11·00	0·1143	9·65	0·1190	9·5	9·2
510	85·60	3·60	10·8	27·25	2·40	7·36	1·38$_8$	3·68	8·80	0·1325	8·85	0·1316	11·0	10·0
610	93·34	2·78	3·88	24·30	2·37	7·33	1·36$_9$	3·67	6·75	0·1818	8·60	0·1361	15·0	10·5
700	95·59	1·96	2·45	22·58	2·36	7·36	1·36$_1$	3·68	6·00	0·2105	9·20	0·1258	17·2	9·7
800	95·86	1·73	2·41	21·89	2·38	7·36	1·37$_5$	3·68	5·79	0·2203	8·90	0·1307	18·0	10·0
900	97·26	1·07	1·67	22·10	—	—	—	—	5·60	0·2229	8·75	0·1333	19·0	10·1
1000	97·37	0·75	1·88	21·46	2·38	7·36	1·37$_5$	3·68	5·35	0·2439	8·75	0·1333	19·9	10·1
1100	97·45	0·76	1·79	21·99	2·38	7·36	1·37$_5$	3·68	5·41	0·2404	8·85	0·1316	19·9	10·0
1200	98·56	0·28	1·16	20·90	2·37	7·36	1·36$_9$	3·68	5·30	0·2469	7·95	0·1493	20·5	11·5
1300	99·27	0·31	0·42	20·90	2·38	7·40	1·37$_5$	3·70	5·15	0·2564	8·6	0·1361	21·1	10·5

* On dry, ash-free basis.

TABLE II.

Analyses, Crystallite Dimensions, and Parameters of Cokes Prepared from Northumberland Coal C. 518 *at* 400—1300°.

Carbonising rate : 250—650°, 2°/min.; 650—900°, 5°/min.

Final carbn. temp.	Ultimate analyses, %.*				Lattice parameter, A.		C–C dist. $=\frac{a}{\sqrt{3}}$, A.	Inter-layer-plane dist. $=c/2$, A.	*a* Axis.		*c* Axis.		Crystallite dimensions, A.	
	C.	H.	N.	S.	*a* axis.	*c* axis.			Line width, *B*, mm.	$1/\beta$.	Line width, *B*, mm.	$1/\beta$.	*a* axis.	*c* axis.
—	82·80	5·35	2·05	0·77	—	—	—	—	—	—	—	—	—	—
400°	83·30	4·16	1·82	0·60	—	—	—	—	—	—	—	—	—	—
450	85·90	3·83	2·22	0·60	2·38	7·02	1·37$_5$	3·51	8·28	0·1422	6·98	0·1745	12·0	13·6
550	89·50	2·60	2·02	0·59	2·38	7·02	1·37$_5$	3·51	6·90	0·1770	6·93	0·1761	14·8	13·6
600	90·70	2·90	2·16	0·56	2·38	7·05	1·37$_5$	3·53	6·55	0·1887	6·88	0·1776	16·0	13·8
650	91·00	2·80	2·24	0·57	—	—	—	—	6·05	0·2083	7·08	0·1745	17·1	13·6
700	93·70	1·89	2·08	0·55	2·38	7·06	1·37$_5$	3·53	5·90	0·2151	6·91	0·1767	18·2	13·7
800	94·14	1·16	1·67	0·56	2·38	7·05	1·37$_5$	3·53	5·59	0·2305	7·20	0·1680	19·3	13·0
900	95·10	1·04	1·50	0·62	2·37	7·07	1·36$_5$	3·54	5·35	0·2439	7·06	0·1751	20·4	13·6
1300	—	—	—	—	2·38	7·08	1·37$_5$	3·54	5·11	0·2591	6·84	0·1789	21·6	13·8

* On dry, ash-free basis.

TABLE III.

Effect of Varying Carbonising Rate upon Composition and Crystallite Dimensions of Cellulose Cokes.

Final carbn. temp.	Analyses, %.*			*a* Axis.			*c* Axis.		
	C.	H.	O (diff.).	Line width, *B*, mm.	$1/\beta$.	Cryst. size, A.	Line width, *B*, mm.	$1/\beta$.	Cryst. size, A.
				Rapid carbonisation.					
400°	80·61	3·66	15·73	—	—	—	—	—	—
500	83·61	2·82	13·52	8·32	0·1414	11·5	8·30	0·1418	10·9
600	88·40	2·67	8·93	8·18	0·1443	11·8	9·75	0·1176	9·1
700	92·17	1·98	5·85	7·27	0·1661	13·8	9·74	0·1178	9·1
800	94·10	1·66	4·24	6·68	0·1842	15·6	9·00	0·1290	10·0
900	95·25	1·02	3·73	—	—	—	—	—	—
1000	96·55	0·78	2·67	5·78	0·2208	18·1	9·30	0·1242	9·6
1100	97·00	0·64	2·36	5·53	0·2340	19·3	8·43	0·1389	10·7
1200	98·35	0·51	1·14	—	—	—	—	—	—
1300	98·80	0·28	0·92	5·32	0·2463	20·3	8·53	0·1370	10·6
				Rapid carbonisation + 5 hours' soaking.					
600	93·04	2·30	4·66	7·20	0·1681	14·0	8·80	0·1325	10·3
900	97·11	0·60	2·29	5·48	0·2364	19·5	8·50	0·1379	10·6
1200	99·09	0·35	0·56	—	—	—	—	—	—
1300	99·41	0·23	0·36	5·13	0·2571	21·2	8·53	0·1374	10·6

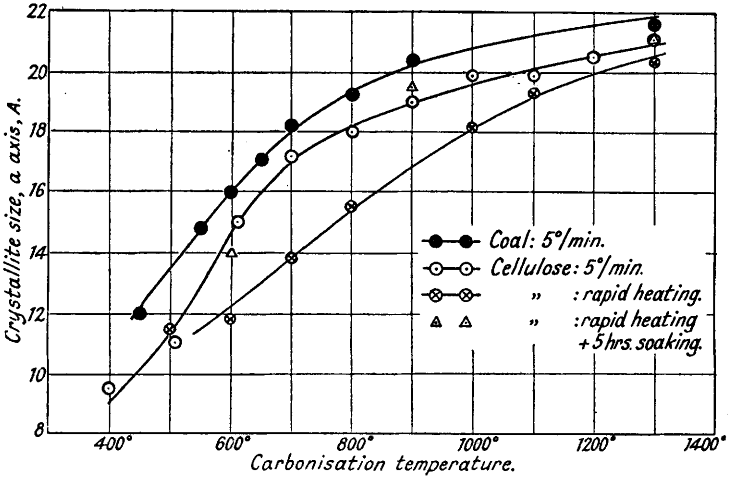
* On dry, ash-free basis.

were converted from hexagonal into orthohexagonal indices, and by using equation (2), the crystallite dimensions in the direction of *a*, *b*, and *c* of the orthohexagonal cell were computed. Since only the $10\bar{1}0$ reflexion (200, 100 orthohexagonal) could be used, the value obtained for the dimension in the direction of the basal planes is a mean value of the *a* and the *b* dimensions. The crystallites can thus be represented as cylinders, the layer planes of the graphite lattice lying parallel to the cylinder base.

The results of the *X*-ray examination and the chemical analyses of the cellulose cokes are shown in Table I. A similar series of results obtained by using a Northumberland coal as the starting material are given in Table II, and the results obtained with different carbonising rates are shown in Table III.

The variation of the *a* dimension of the crystallites with carbonising temperature is shown in Fig. 2.

FIG. 2.



DISCUSSION.

One of the most interesting features of the results is that the *a* dimension of the crystallites shows a continuous growth as the carbonisation temperature increases from 400° to 1300°, whilst the *c* dimension remains practically constant. This means that, whereas the individual hexagon layer planes show a lateral growth during carbonisation, the average number of layer planes in the individual crystallites remains constant. Drastic alterations of the carbonising conditions with respect to the maximum temperature and the variation between wide limits of the rate of heating to that temperature make no difference to the *c* dimension. Apparently, the average number of layer planes in the crystallites is determined by the nature of the starting material, for whereas the cellulose carbon crystallites contain approximately 4 layer planes, the Northumberland coal gives crystallites with an average of approximately 5 planes. This phenomenon is being further investigated.

The change in the *c* spacing with the number of layer planes in the crystallites is also of interest, and confirms Randall's observations (*loc. cit.*). The layer-plane spacing $c/2$ in the cellulose carbon crystallites which possess 4 layer planes is 3·68 A. (see Table I), whereas in the crystallites of the Northumberland coal cokes, which have 5 layer planes, this has decreased to 3·53 A. Some careful measurements on Ceylon graphite, the crystals of which contain a large number of layer planes, gave a value for $c/2$ of 3·3498 A. A 19-cm. camera and chromium-K_α radiation were used for these measurements (cf. Hofmann and Wilm, *loc. cit.*).

The interatomic distance of the carbon atoms in the layer planes is also of interest. Whereas in macrocrystalline graphite it has a value of 1·415 A., in the microcrystalline specimens under investigation it is $1{\cdot}37_5$ A. This value shows no detectable change during the lateral growth of the crystallites from approximately 9 to over 20 A. This result indicates a more powerful bonding of the carbon atoms in microcrystalline graphite than in macrocrystalline graphite. This phenomenon is perhaps connected with the greater degeneracy of the larger hexagon planes in the latter.

It is apparent from Fig. 2 that the lateral development of the hexagon layer planes during carbonisation is a relatively slow process. The values obtained for the *a* dimension of the cellulose carbons prepared by rapid carbonisation are appreciably smaller than those obtained for the carbons prepared by slower carbonisation. The *a* dimensions of the former carbons on being kept at the particular carbonising temperature gradually increase until they reach the dimensions of the latter. The final dimensions reached, therefore, appear to be limiting values.

Another important feature of the results is the relatively rapid lateral growth of the crystallites up to a carbonising temperature of 700°, after which the growth is much slower. This result is of interest because it is at this temperature of 700° that so many abrupt changes occur in the physical and chemical properties of cokes (see "The Solid Products of the Carbonisation of Coal," South Metropolitan Gas Co., 1934; Riley, *Trans. Faraday Soc.*, 1938, **34**, 1011). A difficulty in the way of the exact stoicheiometric interpretation of the *X*-ray results is that they represent average linear dimensions [$(a + b)/2$ and c] of the crystallites present, and we do not therefore know the average shape of the crystallites. If it is assumed that the crystallites approximate to cylinders in shape, then the ratio of the number of unsaturated border carbon atoms relative to the total number of carbon atoms in a single layer plane will be a minimum. On the other hand, this ratio will be a maximum in a layer plane in which all the carbon atoms are border atoms. Free-energy considerations suggest that the former shape is more probable. There is, however, no means of determining to what extent the circular shape is favoured, and therefore for the purpose of this analysis it has been assumed that the actual average shape of an individual layer plane is the arithmetic mean of one in which the above ratio is a minimum and one in which it is a maximum.

Let us picture the process of aromatic condensation occurring during carbonisation, starting at a number of nuclei, the individual layer planes gradually increasing in size until a temperature of approximately 1300° is reached. Little volatile matter then remains in the carbon, and it is therefore highly probable that this process of growth, due to aromatic condensation, is practically complete at this temperature. The work of Ruff, Schmidt, and Ölbrich (*Z. anorg. Chem.*, 1925, **148**, 313), Arndt and Pollack (*ibid.*, 1931, **201**, 81), Wesselowski and Pertzow (*ibid.*, 1934, **216**, 228), Hofmann and Groll (*Ber.*, 1932, **65**, 1257), and Hofmann and Wilm (*loc. cit.*) indicates that in carbon, crystallite growth as a result of thermal recrystallisation does not start below 1400°. The average maximum linear dimension of the layer planes of the cellulose carbon crystallites reached as a result of aromatic condensation will therefore be about 21 A. It is possible on this basis to calculate approximately the amount of excess carbon, hydrogen, and oxygen associated with individual unsaturated border carbon atoms in the form of disordered unsaturated rings and chains in the various cokes. This calculation is given in detail for the 1300° and 400° cellulose cokes.

(i) 1300° *Coke.* (a) *Crystallites assumed cylindrical.*
Diameter of layer plane = 21 A.
Area of layer plane = $\pi r^2 = 346$ A^2.
No. of hexagon rings in a single layer plane = $346/4{\cdot}87 = 71$
No. of carbon atoms = 173
No. of unsaturated border carbon atoms = 33
(b) *Crystallites assumed parallelepipedal.*
$(a + b)/2 = 21$ A.; $a = 2{\cdot}74$ A., therefore $b = 39{\cdot}36$ A.
No. of hexagon rings in a single layer plane = 17
No. of carbon atoms = 70
No. of unsaturated border carbon atoms = 38

Taking the arithmetic mean of the above numbers we obtain for an average single layer plane:

No. of hexagon rings = 44

No. of carbon atoms = 122

No. of unsaturated border carbon atoms = 36

The residue at 1300° represents 20% by weight of the original cellulose. Therefore $122 \times 12 \times 5 = 7320$ g. of the original cellulose were concerned in the formation of a *mole* of the average layer plane in the 1300° crystallites.

(ii) In a similar manner we can calculate from the *X*-ray data the average number of hexagon rings, carbon atoms, and unsaturated border carbon atoms in an average layer plane of the 400° crystallites. If the number of crystallites remains constant throughout the carbonisation, *i.e.*, if no coalescence of nuclei occurs, then 7320 g. of cellulose are concerned in the formation of one *mole* of an average single layer plane of the 400° crystallites. The carbonaceous residue at 400° is 32·62% of the original cellulose and contains 78·45% of carbon (Table I). Therefore the total number of carbon atoms (ordered and disordered) associated with an average layer plane must be

$$7320 \times 0{\cdot}3262 \times 0{\cdot}7845/12 = 156$$

The above calculation shows that the average number of ordered carbon atoms in the layer planes is 38 and the average number of unsaturated border atoms is 18. Therefore the average number of disordered carbon atoms associated with each unsaturated border carbon atom in the crystallites of the cokes prepared from cellulose at 400° must be $(156 - 38)/18 = 6{\cdot}6$.

In a similar manner it can be shown that the numbers of disordered hydrogen and oxygen atoms associated with each unsaturated border carbon atom are 5·4 and 1·45 respectively.

The results of similar calculations carried out for all the cellulose cokes are shown in Table IV. If an attempt is made to draw hypothetical structural formulæ of the layer planes together with the attached disordered rings and chains on the basis of these results and of the valency requirements of the disordered atoms, this can readily be done in the case of the 400° and 500° cokes. With the 700° coke the unsaturated border atoms can only be satisfied if a large and improbable number of triple bonds is assumed amongst the disordered carbon atoms. The possibility of chemical linkage between separate crystallites has been neglected. The picture obtained, however, suggests that in cokes prepared in the region of 700° there are border atoms with their valency requirements unsatisfied. As the carbonisation temperature increases, their number increases, until at 1300°, of 36 unsaturated border atoms in an average layer plane only 5 are attached to hydrogen atoms. Although this interpretation of the *X*-ray results is largely speculative, the general picture obtained is not inconsistent with the changes which occur in other properties during carbonisation; *e.g.*, the development of electrical conductivity at carbonisation temperatures of 600—700° suggests that electrons which have been employed in bonding the disordered atoms at the borders of the hexagon planes become free and confer upon carbon its metallic conductivity. The shrinkage and increase in mechanical strength which occur during carbonisation from approximately 650° upwards

TABLE IV.

Cellulose carbons prepared at 5°/min.

Temp. of coke formation.	Average no. of hexagons in single layer planes.	Average no. of C atoms in single layer planes.	Average no. of unsaturated border C atoms in single layer planes.	Average no. of atoms bound to each unsaturated border C atom.		
				C.	H.	O.
400°	11	38	18	6·6	5·4	1·45
510	14	46	20	4·8	3·6	0·67
610	24	72	26	2·5	1·9	0·17
700	30	88	29	1·5	1·1	0·087
800	33	94	30	1·1	0·92	0·080
900	37	103	32	0·88	0·54	0·053
1000	40	112	34	0·44	0·35	0·054
1100	40	112	34	0·56	0·36	0·053
1200	42	116	34	0·29	0·12	0·031
1300	44	122	36	0·0	0·13	0·011

(Riley, *loc. cit.*) suggest that at this temperature new forces come into play, possibly as a result of the development of a high degree of unsaturation at the borders of the hexagon planes.

Preparation of Carbons.—The carbons employed were prepared by heating the carbonaceous material in an atmosphere of nitrogen. The material (5 g.), in a silica test-tube carrying a thermocouple, was placed in a thin-walled silica tube in an electric furnace. The latter was designed to facilitate temperature control and to ensure a zone of uniform temperature. It consisted of an alundum tube, 12½″ long, 1½″ internal diameter, wound on the inside and the outside walls with Kanthal alloy resistance wire. The two windings could be employed separately or in conjunction. The furnace was lagged with suitably cut, porous fire brick, with an air space between the tube and the lagging. It could be rapidly heated to 1300—1350° (50—60 mins.) and maintained at this temperature for long periods without the use of a reducing atmosphere, with a consumption of about 1·5 kw.

After passage of oxygen-free nitrogen through the apparatus for about 30 mins., the cellulose or coal was dried *in situ* by heating for 30 mins. at 100—110°, after which the temperature was raised at 5°/min. to the desired final temperature. The residue was maintained at this temperature for 10 mins., and the silica tube withdrawn from the furnace and allowed to cool. In the rapid carbonisations, the temperature was increased at approximately 25—30°/min. and the tube and contents were then rapidly cooled by withdrawal from the furnace. The carbons obtained were ground in an agate mortar. The carbon and hydrogen determinations were carried out in duplicate on samples dried in nitrogen at 110—120°.

The authors are indebted to the Metallurgy Research Board of the Department of Scientific and Industrial Research and to King's College Research Committee for grants for the purchase of the *X*-ray apparatus, to the Research Council of the British Iron & Steel Federation for financial assistance, and to the Northern Coke Research Committee in whose laboratory this work has been carried out.

NORTHERN COKE RESEARCH LABORATORY, KING'S COLLEGE (UNIVERSITY OF DURHAM),
NEWCASTLE-UPON-TYNE.

[*Received, November 3rd,* 1938.]