high boiling points and refractive indices. These were probably ketone condensation products but no attempt was made to identify them because of the small quantities available.

There were also indications that isomerization of alkylacetylenes involving migration of the triple bond occurred in contact with the catalyst. Thus the liquid products recovered from an experiment on butyne-1 (b. p. + 8°) contained a small quantity of material which may have been butyne-2 as it boiled at 25–30°, was insoluble in water, gave no reaction with semicarbazide hydrochloride, and turned red on contact with sulfuric acid, as is characteristic of butyne-2.

The materials available were insufficient to show whether pentyne-1 and pentyne-2 isomerized into each other. It is probable that each of these may hydrate to the same ketone without isomerization.

The fact that heptyne-1 hydrated to 4-heptanone is evidence that isomerization of this alkylacetylene occurred before hydration.

The authors are indebted to Mr. G. L. Hervert for assistance in conducting the hydration experiments.

Summary

Catalytic hydration of acetylene and of six alkylacetylenes has been accomplished readily by passing a mixture of the hydrocarbon and steam over a solid phosphoric acid-containing catalyst under atmospheric pressure at 260–300° for acetylene and at 150–204° for the alkylacetylenes.

CHICAGO, ILLINOIS RECEIVED NOVEMBER 10, 1939

[CONTRIBUTION FROM THE LABORATORY OF THE NORTHERN COKE RESEARCH COMMITTEE, NEWCASTLE-UPON-TYNE, ENGLAND]

Crystallite Growth during Carbonization

BY H. E. BLAYDEN, H. L. RILEY AND A. TAYLOR

The following is a description and discussion of further results obtained in a detailed X-ray and chemical study of the changes which occur in the solid phase during the carbonization of various carbonaceous materials. We already have described[1] the results of our study of the carbonization in the temperature range 400–1300° of cellulose and of a Northumberland coal. This work now has been extended in the case of cellulose to 2000° and also to the carbonization of two South Wales anthracites, an American anthracite, lignin and an Irish peat. Although the investigations are still incomplete and because of this their presentation must in some ways be tentative, the results already obtained appear to be of sufficient interest to justify publication at this stage. The demand for new knowledge of this kind need not be emphasized, for the fuller understanding of the molecular mechanism of the combustion and the reactivity of solid carbonaceous fuels demands more complete and fundamental information of their ultimate structure and of the effect of temperature, in the presence and absence of catalysts, upon this structure.

The Hull–Debye–Scherrer method of X-ray analysis has provided a means of obtaining this more detailed information. From the broadening of the diffraction lines in the X-ray powder photographs of the so-called "amorphous" carbons compared with the lines in the X-ray spectrum of macrocrystalline graphite, it is possible to calculate the average dimensions of the crystallites present (assumed to be cylindrical). This method already has been employed for this purpose by Koch-Holm,[2] Lowry and Bozorth,[3] U. Hofmann and co-workers,[4] Berl,[5] Corriez[6] and others. The magnitude of the results reported is affected by the particular method of computation used and to some extent also by the X-ray technique employed. This should be borne in mind when comparing the results of different investigators. The method and technique employed by us, which have already been described in detail,[1] are believed to be in closest keeping with the most recent developments of X-ray crystallographic analysis. Although, in the present state of our knowledge, it is not possible to claim any high order of fundamental accuracy, it is probable

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(1) Blayden, Riley and Taylor, *J. Chem. Soc.*, 67 (1939).

(2) Koch-Holm, *Wiss. Veroff. Siemens Konzern*, **6**, 188 (1927).

(3) Lowry and Bozorth, *J. Phys. Chem.*, **32**, 1524 (1928).

(4) Hofmann and Wilm, *Z. Elektrochem.*, **42**, 504 (1936).

(5) Berl, Andress, Reinhardt and Herbert, *Z. physik. Chem.*, **A158**, 273 (1932).

(6) Corriez, "Contribution à l'étude des variétés noires du carbone," Les Presses Universitaires de France, Paris, 1937.

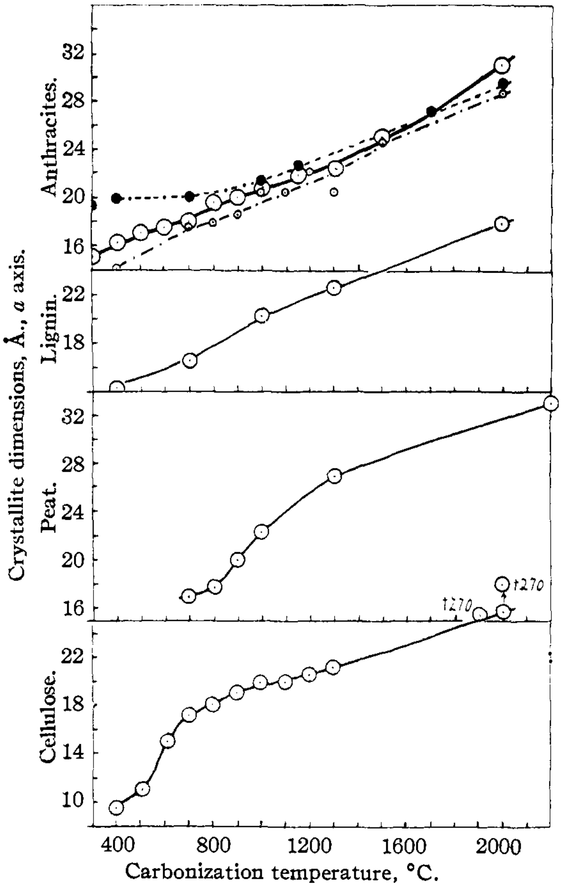


Fig. 1.—The influence of carbonizing temperature on *a* dimensions of crystallites. The results marked t270 for cellulose refer to samples which had been maintained for 270 minutes at the temperature shown. -⊙—⊙-, South Wales anthracite C527; -·⊙-·-⊙·-, South Wales anthracite C607; -⊙---⊙-, American anthracite C618.

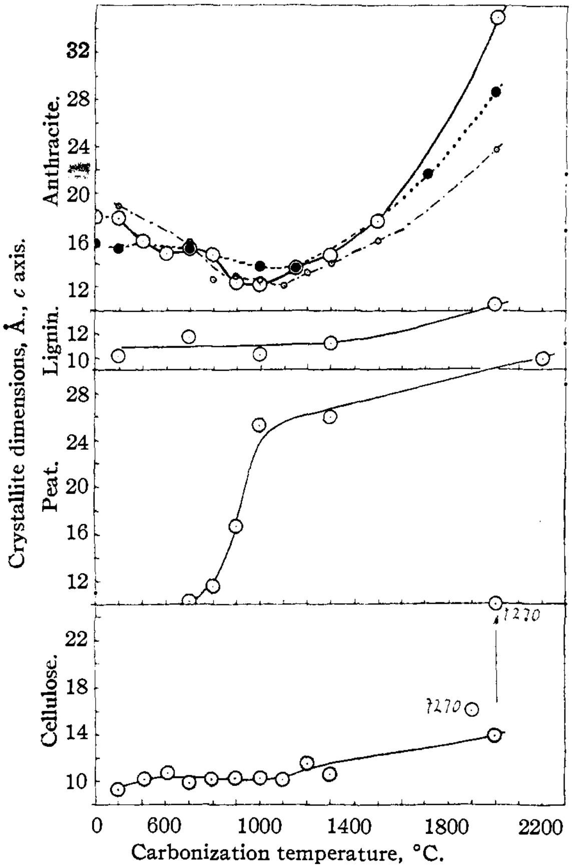


Fig. 2.—The influence of carbonizing temperature on *c* dimensions of crystallites. The results marked t270 for cellulose refer to samples which had been maintained for 270 minutes at the temperatures shown. -⊙—⊙-, South Wales anthracite C527; -⊙-·-·-⊙-, South Wales anthracite C607; -⊙----⊙-, American anthracite C618.

that the results are relatively correct to within 10%.

The general picture of crystallite growth during carbonization which it is possible to form from our own observations and the work of other investigators, particularly U. Hofmann, is as follows. Crystallite growth as a result of processes occurring in the condensed phase with rise of temperature can be divided into three stages. *Stage 1:* from ordinary temperatures to approximately 700°.—In this temperature range the process is essentially one of aromatic condensation or aromatization, the main feature of the growth being the lateral extension of the hexagon layer planes of the graphite crystallites with little or no growth of the crystallites at right angles to the layer planes (*c* direction). That aromatization starts at relatively low temperatures when entirely nonaromatic substances are used has been demonstrated by Smith and Howard.[7] The experiments of Juettner[8] on the formation of mellitic acid from carbon show in a striking way the fundamental significance of 700° in relation to carbonization. *Stage 2:* from 700° to the temperature at which thermal recrystallization commences.—In this temperature range the *c* dimension remains constant and the *a* dimension (average diameter of cylindrical crystallites) increases slowly with rise in temperature. The most obvious explanation of this continued lateral growth of the layer planes appeared to be that the volatile matter still remaining in the carbon at 700° provided the carbon atoms for further aromatization. The results reported in the present paper, however, throw some doubt upon the validity of this

(7) Smith and Howard, THIS JOURNAL, **59**, 234 (1937).

(8) Juettner, *ibid.*, **59**, 1472 (1937).

simple explanation, for when the carbonization is carried to temperatures at which the residue is practically 100% carbon, the linear (*a*) dimensions of the crystallites continue to increase with temperature at the same rate as at lower temperatures. *Stage 3:* from the point at which thermal recrystallization commences upward.—During carbonization, at a more or less definite temperature, the *c* dimension, *i. e.*, the average number of layer planes in the crystallites, begins to increase rapidly. This type of growth which begins in certain cases sharply may be referred to conveniently as "thermal recrystallization," for it undoubtedly involves crystallites growing at the expense of their neighbors. Probably this type of growth is susceptible to "catalytic" influences perhaps due to inorganic substances present. In certain cases it begins at surprisingly low temperatures.

For purposes of comparison we propose to refer to the type of growth shown in the carbonization of cellulose as "normal," *viz.: Stage 1*, more or less rapid increase of the *a* dimension, *c* dimension constant; *Stage 2*, an equal or less rapid increase in the *a* dimension, *c* dimension constant; *Stage 3*, a relatively sharp onset of rapid growth in the *c* direction at a relatively high temperature. We have reason to believe that when growth departs from this "normal" type, extraneous factors are present and in seeking to elucidate these, it is possible that new and fundamental light will be thrown upon the process of crystallite growth and the structure of carbon.

The results obtained in the case of two South Wales anthracites, an American anthracite from the Pennsylvania southern coal field, a lignin prepared from soft wood and an Irish peat, are summarized in Fig. 1 (*a* dimensions) and Fig. 2 (*c* dimensions). The results obtained with cellulose previously reported[1] together with results obtained at higher temperatures, have been included for comparison purposes. Details of the X-ray and analytical results are given in Tables I–V.

Anthracites.—Ten-gram samples of the anthracites, graded between 60 and 100 I. M. M. sieves were carbonized in an atmosphere of nitrogen at 5°/min. up to the required temperature, the product being maintained at the final temperature for ten minutes and allowed to cool in nitrogen. This procedure was adopted for the preparation of cokes up to 1300°. A specially constructed carbon tube resistance furnace which operated in vacuum was employed for the preparation of the cokes at temperatures above 1300°. The rate of heating in this furnace could not be controlled so precisely as in the low temperature furnace as it was necessary occasionally to slow down the rate of heating in order to prevent the powdered charge being blown out of the tube due to the too rapid evolution of gas in the vacuum. The carbons heated to high temperatures in the carbon tube vacuum furnace were given a preliminary carbonization in nitrogen up to 1000° in the wire resistance tube furnace. In order to prevent the appearance of lines due to ash on the X-ray photograph the samples were thoroughly extracted after carbonization by boiling with 20% hydrochloric acid followed by two evaporations with hydrofluoric acid, then by another treatment with hydrochloric acid. This was usually sufficient to reduce the amounts of crystalline ash constituents to such an extent that no trace of ash lines was visible on the powder photographs. The coals and cokes after this treatment contained appreciable amounts of very firmly adsorbed hydrochloric acid (*vide infra*). To remove this it was necessary to heat the sample in vacuum to 110°. Duplicate chemical analyses were made and powder photographs taken from which crystallite dimensions were computed by the method already described.

The *a* dimension-carbonizing temperature curves obtained with these anthracites are interesting in several respects. In stage 1, the anthracite curves are consistently higher than the bituminous coal curve already reported. It is noteworthy that the American anthracite itself (95.92% C) and the cokes prepared from it up to 700° all give *a* dimensions greater than the corresponding samples prepared from the two Welsh anthracites (92.50 and 93.64% C). These results are in accord with the views of Bone and coworkers and others upon the relationship between coal rank and the development of "benzenoid" characteristics. Another interesting feature which could perhaps have been anticipated from the experiments of Juettner[8] is that the crystallite *a* dimensions for the two Welsh anthracite 700° cokes (18.0 and 17.6 Å.) and the *a* dimension of a corresponding bituminous coal coke crystallite

TABLE I

EXAMINATION OF S. WALES ANTHRACITE C527

Analysis of C527: ash, 1.0 (dry coal basis); C, 93.64; H, 2.75 (dry, ash-free basis).

Carbonization temp., °C.	Analysis (dry, ash-free basis)		Crystallite size, Å.		Inter-atomic dist., Å.	Inter layer plane dist., Å.
	C, %	H, %	*a*-axis	*c*-axis		
400	92.35	2.80	16.3	17.8	1.38	3.41
500	92.36	2.76	16.6	15.9	1.38	3.44
600	92.40	2.50	17.6	14.9	1.38	3.45
700	92.38	2.25	18.0	15.4	1.38	3.50
800	93.40	1.54	19.6	14.8	1.38	3.54
900	94.10	0.84	20.0	12.4	1.38	3.52
1000	94.74	.83	20.6	12.3	1.38	3.60
1150	96.90	.46	21.8	13.7	1.38	3.55
1300	98.32	.23	22.4	14.8	1.37	3.46
1500	..	..	25.0	17.6	1.39	3.47
2000	99.44	..	31	35	1.41	3.38

TABLE II

EXAMINATION OF S. WALES ANTHRACITE C607

Analysis of C607: ash, 4.0 (dry coal basis); C, 92.50; H, 3.37 (dry, ash-free basis).

Carbonization temp., °C.	Analysis (dry, ash-free basis) C, %	H, %	Crystallite size, Å. a-axis	c-axis	Interatomic dist., Å.	Inter layer plane dist., Å.
400	92.20	3.20	14.2	19.0	1.38	3.40
700	93.12	2.37	17.6	15.7	1.38	3.45
800	94.34	1.55	18.0	12.7	1.38	3.53
900	95.34	0.97	18.7	12.8	1.38	3.60
1000	95.84	.63	20.6	12.6	1.38	3.60
1100	96.66	.44	20.5	12.2	1.38	3.54
1200	97.76	.28	22.2	13.3	1.39	3.60
1300	97.82	.18	20.5	14.0	1.38	3.59
1500	98.56	.05	24.8	16.0	1.39	3.51
2000	99.26	..	28.7	23.8	1.40	3.41

TABLE III

EXAMINATION OF AMERICAN ANTHRACITE C618

Analysis of C618: ash, 2.95 (dry coal basis); C, 95.92; H, 1.93 (dry, ash-free basis).

Carbonization temp., °C.	Analysis (dry, ash-free basis) C, %	H, %	Crystallite size, Å. a-axis	c-axis	Interatomic dist., Å.	Inter layer plane dist., Å.
400	95.96	1.67	20.0	15.4	1.39	3.44
700	95.70	1.61	20.0	15.4	1.38	3.43
1000	..	..	21.4	13.8	1.39	3.54
1150	98.14	0.40	22.6	13.7	1.39	3.53
1700	99.62	..	27.6	21.5	1.39	3.44
2000	..	..	29.6	28.5	1.40	3.42

(18.2 Å.) are approximately the same while the American anthracite 700° coke gives a value only slightly greater (20.0 Å.). It is also perhaps significant that in stage 2, the growth curves of all four coals are approximately concurrent.

As far as our knowledge goes at present it would appear that the extent to which the lateral growth of a crystallite can occur in the earlier stages of carbonization must be governed primarily by two factors, *viz.* (1) the number of graphite nuclei present in the parent material or formed during carbonization, around which aromatic condensation occurs, and (2) the chemical nature of the carbonaceous material, *e. g.*, substances containing much oxygen would be expected, when carbonized, to give off a larger proportion of volatile matter and, other things being equal, to form smaller crystallites. The remarkable similarity of the *a* dimension of the 700° coke crystallites prepared from quite diverse substances suggests that other and possibly more fundamental factors control crystallite growth in stage 1.

The *c* dimension growth curve (Fig. 2) shows a very different state of affairs from that obtaining with the cellulose, lignin and Northumberland coal. Whereas with the latter the *c* dimension remains constant over a considerable range of carbonizing temperature this is not so with the anthracites. The Welsh anthracite crystallites contain on the average 6 layer planes and the American anthracite 5.6. At a carbonizing temperature of 400° the *c* dimension begins to decrease and at 900° reaches a value corresponding to an average of approximately 4.5 layer planes. As the temperature is further increased the crystallites show a pronounced growth in the *c* direction. This phenomenon is not quite so pronounced with the American as with the Welsh anthracites.

It already has been pointed out[1] that the *c* spacing is an inverse function of the *c* dimension. This fact provides an interesting and independent check of the crystallite size determinations. In Fig. 3, *c* dimension has been plotted against *c* spacing for a large number of crystallites and it will be seen that the anthracite results fall on a smooth curve drawn through these points.

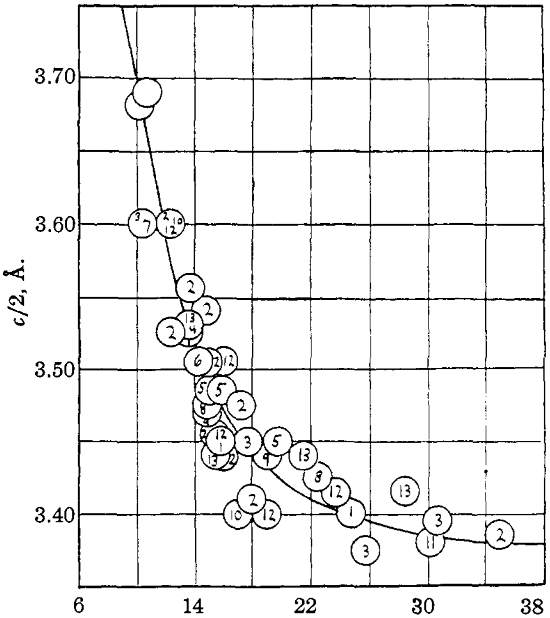
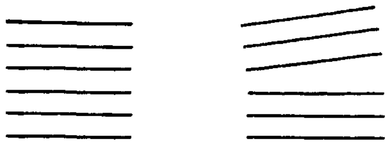


Fig. 3.—Variation of interplanar distances with crystallite size in *c* direction: 1, cellulose carbons; 2, S. W. anthracite C527; 3, peat; 4, coke C518; 5, coke C383; 6, lignin; 7, wood; 8, coke C526; 9, coke C528; 10, coke C458; 11, pentadiene carbon; 12, S. W. anthracite C607; 13, American anthracite C618.

It is apparent from Fig. 1 that the lateral growth of the layer planes as the temperature increases is much too small to account for the decrease of the *c* dimension by the lateral growth of certain of the layer planes at the expense of others. The most probable explanation appears to be that rise of temperature causes disruption of the original anthracite crystallites in the manner shown in Fig. 4. It is possible that this phenomenon is connected with the decrepitation which occurs when many anthracites are heated rapidly, for if the above explanation is correct then rise of temperature will be accompanied by a disruption of the crystallites and a consequent anisotropic expansion along the *c*-axis which would be sufficient to cause decrepitation.



(a) Original anthracite layer planes.

(b) Probable disorder introduced into the anthracite crystallite by heating to 500–900°.

Fig. 4.

The question naturally arises as to why this crystallite disruption occurs with the anthracites studied and not with the Northumberland coal and several other bituminous coals upon which preliminary tests have been made. Although a much greater number of coals must be examined before this question can be answered, the following points are worthy of consideration. Theoretical considerations have been advanced[9] which indicate the possibility of bonding hydrogen atoms or ions between the layer planes of the graphite crystal lattice. Anthracite has been reported to have an adsorptive power greater than coals of lower rank for both carbon dioxide[10] and methane.[11] These facts suggest that the disruption of the anthracite crystallites on heating, may be connected with the desorption of interstitially adsorbed gas, probably hydrogen. The fact that gas evolution and crystallite disruption commence at approximately the same temperature supports this hypothesis.

Lignin.—The lignin used was prepared from soft wood sawdust by Klason's method[12] and cokes were made from it in the manner already described. It will be seen from Fig. 1 that in stage 1 the lignin coke crystallites show an *a* dimension growth curve very similar to that of the anthracites. This is probably a reflection of the fact that the lignin itself contains highly condensed aromatic molecules[13] arranged in a lattice which must in many respects be similar to that of a graphite crystallite.[14]

TABLE IV

EXAMINATION OF LIGNIN

Analysis of lignin: ash, 0.59 (dry basis); C, 65.70; H, 4.57 (dry, ash-free basis).

Carbonization temp., °C.	Analysis (dry, ash-free basis) C, %	H, %	Crystallite size, Å. *a*-axis	*c*-axis	Inter-atomic dist., Å.	Inter layer plane dist., Å.
400	76.01	3.38	14.3	10.3	1.38	3.60
700	91.72	1.73	16.6	11.8	1.38	3.69
1000	96.62	0.57	20.4	10.4	1.37	3.69
1300	98.90	.20	22.6	11.2	1.37	3.75
2000	..	..	27.9	14.3	1.40	3.51

In other respects the lignin crystallite growth curves can be considered normal. The preparation of lignin involved the extraction of wood with strong mineral acid which removed not only the cellulose but also the major part of the inorganic constituents. The cokes were thus prepared from a material relatively low in ash. This is probably connected with the fact that thermal recrystallization as evidenced by the rapid increase of the *c* dimension only sets in at relatively high temperatures (*vide infra*).

Peat.—The Irish peat employed was from Turraun, and its properties already have been described in detail.[15] Owing to its ash content and the difficulty of eliminating this from the cokes prepared at low temperatures by acid extraction, it has not yet been possible to prepare X-ray photographs, for stage 1 of the growth curves, sufficiently free from ash lines to permit of their use in crystallite size determinations. The results recorded are from 700° upward. The growth curves are entirely anomalous. The growth of the *a* dimension between 700 and 1300° is considerably greater than that recorded for the other materials studied. More surprising is the rapid growth of the *c* dimension which occurs between 700 and 1000°. This is not an isolated result. Preliminary experiments have shown that

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(9) Balfour, Riley and Robinson, *J. Chem. Soc.*, 456 (1936). See also Lowry, THIS JOURNAL, **46**, 824 (1924); *J. Phys. Chem.*, **33**, 1332 (1929).

(10) Sinkinson and Turner, *Ind. Eng. Chem.*, **18**, 602 (1926).

(11) Coppens, *Ann. Min. Belg.*, **37**, 173 (1936).

(12) Klason, *Chem. Rev.*, **14**, 117 (1934).

(13) Fuchs, *Brennstoff-Chem.*, **9**, 178 (1928); Fischer, *Abh. Kohle*, **6**, 277 (1923).

(14) Sedletzky and Brunowsky, *Kolloid Z.*, **73**, 90 (1935).

(15) D. S. I. R., Fuel Research Board, Technical Paper No. 4,

other Irish peats behave similarly. Two explanations of this phenomenon suggest themselves. The anomalous growth may be due to either (a) something inherent in the organic structure of the peat material or (b) a catalytic effect. (a) appears unlikely for the following reasons: (1) the anomalous growth in the *c* direction is not shown by cellulose, lignin or a sample of soft wood; (2) the X-ray photographs of the cokes give no indication that their organic structures are fundamentally different from those of other carbonaceous materials; (3) the anomalous growth is not prevented by carbonizing in high vacuum instead of nitrogen. The evidence in favor of (b) is as follows: (1) the ash content of the peat is higher than that of the other carbonaceous materials employed; (2) the ash is probably intimately associated with the organic matter, for acid extraction fails to remove it completely; (3) the carbonaceous material remaining after extraction of the original peat with boiling concentrated or dilute (2%) hydrochloric acid behaves normally and does not show the rapid growth in the *c* direction at low temperatures. Such treatment might, however, besides extracting ash, also bring about an alteration in the nature of the organic matter present; (4) attempts to promote growth in the *c* direction at low temperatures by the pretreatment of ash-free cellulose with iron and alkali salts so far have been unsuccessful. At higher temperatures (1600°), inorganic additions have a very pronounced effect, promoting very rapid growth.[16] Details of these experiments will be published at a later date.

TABLE V

EXAMINATION OF IRISH PEAT C445

Analysis of Irish peat: ash, 3.5 (dry basis); C, 57.22; H, 5.27 (dry, ash-free basis).

Carbonization temp., °C.	Analysis (dry, ash-free basis)		Crystallite size, Å.		Interatomic dist., Å.	Inter layer plane dist., Å.
	C, %	H, %	*a*-axis	*c*-axis		
400	76.35	3.92	..	..	..	..
700	90.12	1.76	17.0	10.3	1.38	3.60
800	91.80	1.20	17.8	11.5	1.38	3.58
900	93.88	0.68	20.0	16.7	1.39	3.45
1000	95.70	.56	22.4	25.2	1.39	3.36
1300	97.94	.27	27.4	25.8	1.39	3.38
2200	99.4	..	32.8	30.8	1.38	3.39

Although at present it is not possible to put forward a definite explanation of this phenomenon, these results suggest the possibility of rendering the carbon atoms in the graphite crystallites highly mobile at relatively low temperatures with a consequent enhancement of their reactivity.[17]

The pronounced falling off in the rate of growth in the *c* direction at 1000° may be due either to (a) the elimination of the catalyst by volatilization or (b) change in the degree of contact of individual crystallites, brought about by the pronounced growth which already has occurred.[18]

Crystallite Growth at High Temperatures.—With temperatures up to 1300°, a carbonization rate of 5° per minute and heating for ten minutes at the final temperature provides sufficient time for maximum growth. No appreciable further growth was detected when cellulose cokes were heated for an additional period of five hours at the maximum temperature. The nature of the growth occurring at temperatures greater than 1600° may be of a different character from that occurring at lower temperatures. The results obtained with cellulose show that after carbonizing at 5° per minute the retention of the specimen at the final temperature for several hours brings about considerable further crystallite growth.

The form of the *c* dimension curves of the anthracites, which were carbonized in the presence of their ash, compared with the corresponding curves for cellulose and lignin both of which were subjected to a preliminary acid extraction, suggests that the inorganic constituents must play an important role in the growth process at high temperatures.

The Adsorption of Hydrochloric Acid by Coals and Cokes.—The anomalous nature of the ultimate analyses of the cokes prepared from the anthracites after extraction with hydrochloric and hydrofluoric acids led us to investigate the adsorption of hydrochloric acid by these substances. It was discovered that both the coals and the cokes adsorb considerable quantities of hydrochloric acid which is not eliminated by several hours of heating in vacuum at 110°. That this adsorbed hydrochloric acid replaces some of the inherent water in the air dried coals is shown by the following results.

	%
(a) Increase in weight of anthracite after extraction with hydrochloric acid	2.11 (dry coal basis)
(b) Chlorine content of anthracite after extraction with hydrochloric and hydrofluoric acids	2.28 (dry coal basis)

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(16) *Cf.*, however, statements of Arsem, *Trans. Am. Electrochem. Soc.*, **20**, 105 (1911).

(17) *Cf.* investigations of Hedvall, *Z. Elektrochem.*, **45**, 83 (1939).

(18) Wesselowsky and Pertzov, *Z. anorg. Chem.*, **216**, 228 (1934).

	%
(c) Moisture content of the air dried anthracite before extraction with hydrochloric acid	2.5
(d) Moisture content of the air dried anthracite after extraction with hydrochloric acid	0.5

The hydrochloric acid contents of a series of cokes after extraction with this acid and subsequent drying at 110° are shown in Table VI.

TABLE VI

ADSORPTION OF HYDROCHLORIC ACID

Carbonization temp., °C.	HCl adsorbed, % of dry substance Anthracites C527	C607	Lignin	Irish peat
400	0.83	1.50	0.43	2.38
500	1.07	..	..	..
600	0.72	..	..	..
700	.59	1.60	.74	3.18
800	.51	1.45	..	1.96
900	.72	1.51	..	0.91
1000	.09	0.71	.04	.92
1100	..	.49	..	..
1150	.19	..	..	..
1200	..	.06	..	..
1300	..	..	Trace	1.18

It will be seen (Table VI) that the amount of adsorbed hydrochloric acid passes through a maximum with the 700° coke, which is significant in view of the results of other investigations on adsorptive power.[7]

Dotted line is value for macro-crystalline graphite.

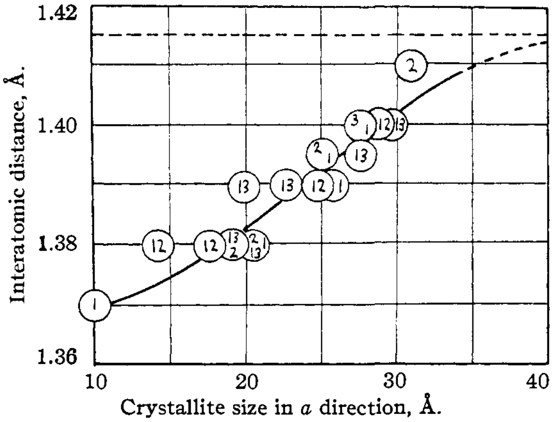

Fig. 5.—Variation of interatomic distances with crystallite size in *a* direction: 1, cellulose carbons; 2, S. W. anthracite C527; 3, peat; 4, coke C518; 5, coke C383; 6, lignin; 7, wood; 8, coke C526; 9, coke C528; 10, coke C458; 11, pentadiene carbon; 12, S. W. anthracite C607; 13, American anthracite C618.

Variation of C–C Spacing with Crystallite Size.—It already has been pointed out that the *c* spacing is an inverse function of the number of layer planes in the crystallite. The C–C spacing in the layer planes also shows an interesting variation with crystallite size. The C–C spacing in the layer planes of macrocrystalline graphite is 1.415 Å., while in the microcrystalline carbons already studied it is approximately 1.37–1.38 Å. The measurements recorded in this paper indicate that the latter value increases as the crystallites grow. Figure 5 shows the C–C spacing plotted against the *a* dimension of the layer plane.

Conclusion.—It is apparent from the above results that investigations of this kind are likely to throw considerable light upon the ultimate nature of coals and "amorphous" carbons and upon the changes which these substances undergo on heating. The investigation already has revealed a number of quite unexpected results and it would therefore at this stage be unwise to theorize as there is still a host of very diverse carbonaceous materials, both synthetic and natural, to be studied.

The authors are indebted to the Northern Coke Research Committee for permission to publish this paper, to Dr. F. S. Sinnatt (Director, Fuel Research Board, D. S. I. R.) and the Amalgamated Anthracite Co., Wales, for samples of peat and anthracite, respectively, and to Dr. A. C. Fieldner (U. S. Bureau of Mines) and the Lehigh Navigation Coal Co., Pa., for samples of the American Anthracite. They also record their thanks to Messrs. J. Gibson, B. Sc. and J. Almond for assistance with the analyses.

Summary

The investigations of crystallite growth during carbonization in the temperature range 400–1300°[1] have now been extended to include one American and two Welsh anthracites, lignin and an Irish peat, and carbonization temperatures up to 2200°. The anthracites and the peat all show interesting anomalies in their crystallite growth curves. The anthracite crystallites show a decrease in the *c* dimension as the carbonization temperature is increased from 400 to 900°. This has been interpreted as due to disruption of the crystallites. The peat coke crystallites show a very rapid growth in the *c* direction between 700 and 1000° which is probably due to a catalytic effect.

The significance of the results obtained is discussed in detail.

NEWCASTLE-UPON-TYNE, ENGLAND

RECEIVED SEPTEMBER 18, 1939