406. *Studies in Graphite Formation. Part I. The Estimation of Graphite.*

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It is now widely recognised that carbon exists in only two allotropic modifications, *viz.*, diamond and graphite, the so-called " amorphous " forms containing appreciable quantities of volatile impurities, particularly hydrogen, which have a pronounced effect upon the properties. The change " amorphous " carbon→graphite is in no sense an allotropic or a monotropic change, but probably the high-temperature pyrolysis of complex, very stable hydrocarbons to form, in the limit, pure carbon in the form of graphite.

Hitherto three methods have been employed for the estimation of graphite in the presence of amorphous carbon : (1) oxidation of graphite to " graphitic acid " by a mixture of nitric and sulphuric acids and potassium chlorate; (2) measurement of physical properties, particularly the electrical conductivity; (3) *X*-ray examination. None of these methods is free from objection. The vigorous nature of the oxidising agent renders the results obtained by (1) unreliable, and, according to Hoffmann and Frenzel (*Ber.*, 1930, **63**, 1248), every variety of carbon can be converted into graphitic acid if it has a pure carbon surface and is sufficiently finely divided. The precise measurement of the electrical conductivity of carbon presents many practical difficulties. Owing to the porous nature of the material, it is necessary to employ a finely divided sample, and the results must be considerably affected by the shape and surface conditions of the particles and by the pressure to which the powder is subjected. The size and orientation of the crystallites of graphite in the sample also affect the conductivity (Arndt and Pollack,* *Z. anorg. Chem.*, 1931, **201**, 81; Nishiyama, *Sci. Rep. Tohoku*, 1932, **21**, 171). It has also been shown (Siebel, *Z. Physik*, 1921, **4**, 288) that the electrical resistance of carbon is increased slightly by simple exposure to air. The fact that the presence of very small amounts of hydrogen in carbon has very pronounced effects, makes the exact interpretation of *X*-ray spectra difficult and indecisive. Of these methods, the second probably offers the most reliable guide to the extent of graphite formation in a sample of amorphous carbon.

It is not unlikely that, at temperatures high enough to bring about the formation of an appreciable number of oxygen ions, the ionic nature of the graphite crystal lattice plays a very important part in determining its velocity of combustion. Sihvonen (*Suomen Kem.*, 1935, **8**, *B*, 26) has shown that oxygen, under low pressures, " activated " by *X*-rays or by an electric discharge, does not react with diamond (covalent crystal lattice) but does so with graphite, forming carbon monoxide and dioxide—a reaction probably connected with the ionic nature of the lattice, for graphite is very unreactive to molecular oxygen. Highly graphitised fuels, such as retort carbon, are known to give much higher combustion temperatures than fuels containing less graphite. A means whereby the graphite content of samples of carbon could be determined would therefore be of value in the study of fuel economy in blast furnaces and cupolas. It would also provide a means of characterising samples of carbon, which would be of service in the study of, *e.g.*, the respective parts played by graphite and " amorphous " carbon in sorption phenomena (cf., *inter alia*, Bangham and Stafford, J., 1925, **127**, 1085; Lowry, *J. Amer. Chem. Soc.*, 1924, **46**, 824; King, *Trans. Faraday Soc.*, 1935, **31**, 935), the extent to which the nature of the original carbonaceous compound determines the amount of graphite formed on pyrolysis (cf. Ciusa, *Gazzetta*, 1922, **52**, ii, 130; 1925, **55**, 385; 1928, **58**, 222; Bellino, *ibid.*, 1932, **62**, 795), and the effect of temperature and other variables upon the formation of the ionic graphite lattice from the covalent " amorphous " carbon lattice.

The present series of papers will be concerned with these problems, and this part deals with a method of estimating graphite which, although subject to certain limitations, possesses advantages over the electrical conductivity method in that reproducible results are readily and simply obtained. Uncertainties in the interpretation of the results arise in dealing with samples of carbon of widely different densities and physical form, but with similar types of carbon, the method appears to give a reliable indication of the relative amounts of graphite present. The method, which has already been outlined (Blayden and Riley, *J. Soc. Chem. Ind.*, 1935, **54**, 159T), consists in measuring the rate of oxidation at 100° of the finely ground and accurately graded samples of carbon by a solution of potassium dichromate in syrupy phosphoric acid, by which those forms of carbon which are known to be highly graphitised, *e.g.*, natural graphite, electrode carbons, retort carbon, etc., are oxidised much more rapidly than sugar charcoal prepared at approximately 900°. The extreme types of carbon so far examined by this method gave the following results. 1 G. of charcoal, graded between 60 and 100 I.M.M. sieves and prepared by carbonising sucrose slowly up to 900°, gave, under the standard conditions, only 16 mg. of carbon dioxide in 2½ hours, whereas 1 g. of a similarly graded sample of a graphite electrode carbon † gave, under similar conditions, 1600 mg. Diamond gave only 43 mg. in 2½ hours. It is remarkable that the graphitic carbon, which is so much less reactive to gaseous oxygen than sugar charcoal, should be oxidised so much more rapidly, in spite of the greater area which the less dense sugar charcoal presents to the oxidising solution.

Since, ionic reactions proceed much more rapidly than those involving activation of

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* These authors employ the term " graphitisation " to denote both the original formation of graphite by the decomposition of an organic compound, and also the grain growth at higher temperatures. The word is here employed in its chemical sense.

† Origin unknown, but probably prepared by heating artificial graphite together with a carbonaceous binder at a high temperature for a prolonged period. The sample had a high electrical and thermal conductivity.

molecules, Blayden and Riley (*loc. cit.*) suggested that in the reaction of carbon with molecular oxygen we are dealing with a molecular reaction in which the impurities present in the carbon act as reaction centres, whereas in the wet oxidation of carbon, we are dealing with an ionic reaction. It has now further been shown that the phosphoric acid plays a very important part in differentiating, by means of the reaction velocity, between "amorphous" and graphitic carbon. Figs. 1 and 2 show the effect of phosphoric acid concentration on the velocity of oxidation of electrode carbon and of sugar charcoal by the above method. With the former, the reaction velocity was reduced to approximately one-thirteenth of its original value when water, instead of syrupy phosphoric acid, was employed as solvent for the chromic acid; with sugar charcoal, no such change was observed, but the reaction velocity showed a minimum value when the chromic acid solvent was 50% syrupy phosphoric acid and 50% water. The dependence of reaction velocity upon phosphoric acid concentration is illustrated in Fig. 3. In the absence of phosphoric acid, *i.e.*, with a solution of chromic acid in water, the electrode carbon and the sugar charcoal were oxidised at approximately the same rate. A concentrated sulphuric acid solution showed similar, but not such great, differences in the oxidation velocities (see below).

FIG. 1.

Electrode Carbon.

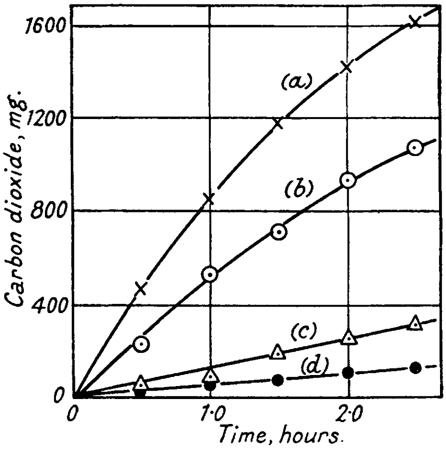
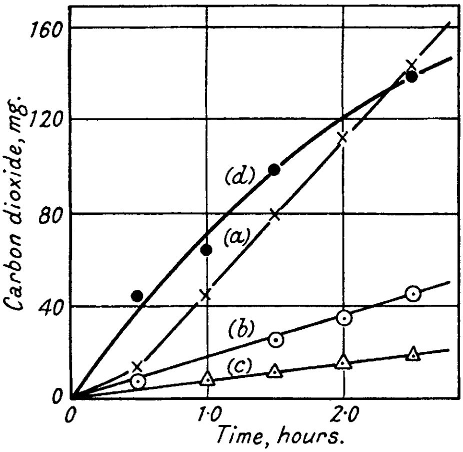


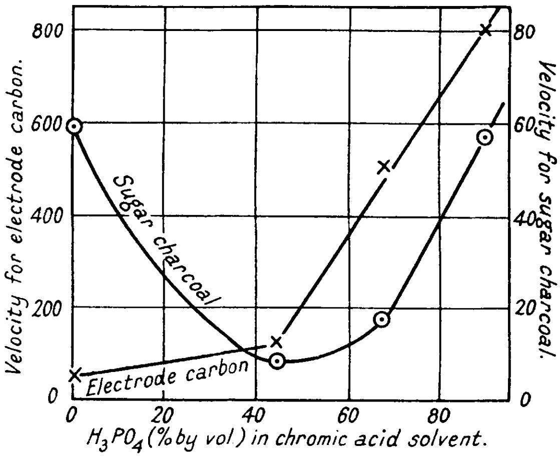
FIG. 2.

Sugar Charcoal.



50 *C.c. of oxidising solution, prepared as follows, used in each oxidation:* 13·6 *g.* H_2CrO_4 *dissolved in* (a) 100 *c.c. syrupy* H_3PO_4 (d, 1·75); (b) 75 *c.c. syrupy* H_3PO_4 + 25 *c.c.* H_2O; (c) 50 *c.c. syrupy* H_3PO_4 + 50 *c.c.* H_2O; (d) 100 *c.c.* H_2O.

FIG. 3.



Oxidising solution.	Mg. CO_2 in 2½ hrs. Electrode carbon.	Sugar charcoal.
3·55 G. $K_2Cr_2O_7$ in 50 c.c. conc. H_2SO_4	205	40
3·55 G. $K_2Cr_2O_7$ in 50 c.c. syrupy H_3PO_4	679	93

Chromic acid is less soluble in concentrated sulphuric acid than in syrupy phosphoric acid, so for comparative purposes less concentrated solutions were employed. Bartoli and Papasogli (*Gazzetta*, 1883, **13**, 37) have shown that, when graphite is anodically oxidised, the chief products are carbon monoxide and dioxide and "graphitic acid" ($C_{14}H_2O_3$). When, however, phosphoric acid was employed as the electrolyte, they obtained a "graphitic acid" containing phosphorus. This result indicates that phosphoric acid can, under certain conditions, react chemically with graphitic carbon. The following simple experiment lends further support to this view.

An arc-electrode carbon was broken in two and the pieces used as anodes in two electrolytic cells connected in series, one containing 10% aqueous phosphoric acid and the other 10% aqueous sulphuric acid. A current of approximately 80 milliamps./cm.^{2} of the anode surface was passed through the cells. After 20 minutes the first cell contained a concentrated colloidal dispersion of a dark carbonaceous substance ("phosphorus graphitic acid"?), whereas the electrolyte in the second cell remained almost clear. The phenomenon, which is being investigated further, suggests that the specific action of phosphoric acid in the chromic–phosphoric acid oxidations could be accounted for by a direct chemical attack or a peptising action on the graphite by the phosphoric acid. This acid itself does not attack graphite appreciably at 100°, so presumably the chemical or peptising action only occurs, or is greatly accelerated, when the graphite is being oxidised. This would offer a reasonable explanation of the greater susceptibility of graphite than of amorphous carbon to oxidation, *viz.*, a chemical or dispersing action of the phosphoric acid upon graphitic (but not upon amorphous) carbon, followed by a rapid oxidation of the product.

If samples of coal are carbonised over a range of temperatures, then in the neighbourhood of 700° there is a critical temperature at which profound changes in the properties of the coke samples occur (see "The Solid Products of the Carbonisation of Coal," 1934, 59; South Metropolitan Gas Co.): "The contraction in volume, the large increase in electrical conductivity, the decrease in reactivity to sulphuric acid, the loss of ability to be dispersed in sulphuric acid, the attainment of and fall from maximum adsorptive power, the rise in ignition temperature and fall in combustibility all point in this direction" (see also Arndt and Pollack, *loc. cit.*). Burgess and Wheeler (J., 1910, **97**, 1917) showed that at temperatures above 700°, the gases evolved during the carbonisation of coal are chiefly hydrogen, accompanied at first by a little methane; and Stock, Lux, and Rayner (*Z. anorg. Chem.*, 1931, **195**, 158) proved that at temperatures higher than 750° hydrogen is the principal impurity remaining in degassed charcoal. If it be accepted that "amorphous" carbon is a complex hydrocarbon containing a small quantity of hydrogen, arranged in such a way, in the ideal case, that the lattice is completely covalent, then the above facts are readily interpreted by the following view. At the critical temperature, in the neighbourhood of 700°, the decomposition of the covalent "amorphous" carbon commences, with the reduction of its hydrogen content and the progressive formation of the metallic graphite lattice, with a consequent fundamental alteration in both chemical and physical properties.

The existence of this critical temperature near 700° is further illustrated by the susceptibility of specimens of carbon, prepared over a range of temperature, to oxidation by the chromic–phosphoric acid solution. A series of cokes, prepared from each of three different coals by carbonisation in nitrogen for one hour at different temperatures, were submitted to the standard wet oxidation test, and the results are shown in Fig. 4, velocity of oxidation being plotted against carbonisation temperature. The three curves obtained from (*a*) steam coal, (*b*) a coking coal, and (*c*) an anthracite all show a pronounced minimum at about 650°. The wet oxidation rates depend partly upon the manner in which the carbonisation is carried out, but the minimum at 650° is a definite characteristic of the curves. The maximum at 450° in curve (*b*) is connected with the coke-forming properties of the coal, and will be discussed elsewhere. That the cokes formed at temperatures greater than 700° show, with increased temperature of carbonisation, an increased susceptibility to oxidation appears to indicate that graphitisation commences in the neighbourhood of this temperature. This view is supported by other pronounced changes which occur at the same temperature. In Fig. 5 both the volatile-matter contents of the cokes prepared from the coal (*b*) and the amounts of water vapour sorbed from a partially saturated atmosphere are plotted against the carbonisation temperatures: the pronounced changes in the neighbourhood of 650° are obvious (compare the results obtained by the South Metropolitan Gas Co., *op. cit.*, for the sorption of carbon dioxide).

Bangham and Stafford (*loc. cit.*) showed that graphite does not sorb molecular hydrogen but can be made to take up hydrogen (ionic) in a discharge tube; the graphite was in this way " activated " and would now sorb oxygen. This result is in accord (1) with the fact that increase in wet oxidation rate (*i.e.*, an increase in graphite content) is accompanied by a decrease in sorptive capacity at temperatures of carbonisation over 700°; and (2) with the view that the change " amorphous " carbon→graphite consists essentially in the elimination of hydrogen from a hydrocarbon complex.

The above results leave little doubt that the rate of oxidation of finely ground, closely graded samples of carbon, by the chromic–phosphoric acid solution, gives a semi-quantitative measure of the extent to which the sample is graphitised. The method is, of course, open to uncertainties due to lack of means of measuring the surface area of carbon particles.

FIG. 4.

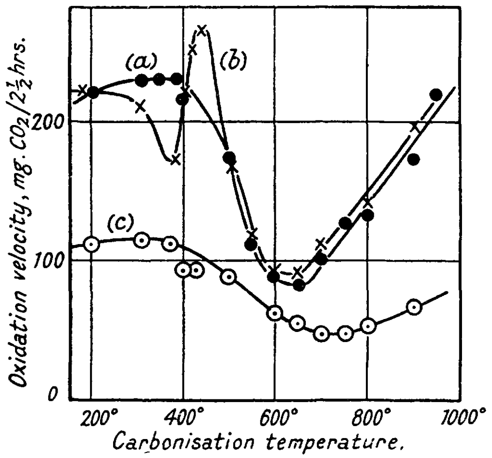
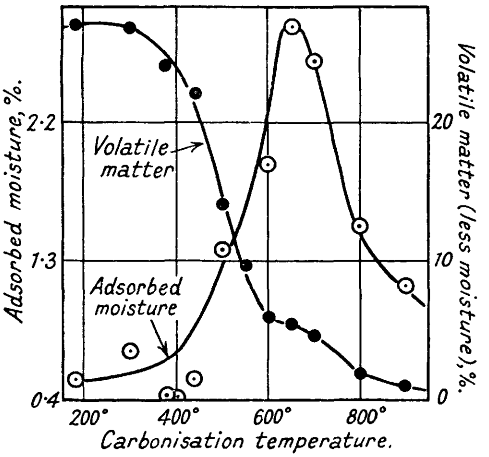


FIG. 5.



It is, however, highly significant that it is the denser graphitic carbon (generally supposed to have a less porous surface than other forms of black carbon) which is the more rapidly oxidised.

EXPERIMENTAL.

The standard method employed in measuring the oxidation velocities (see Blayden and Riley, *loc. cit.*) consisted essentially in oxidising at 100° 1 g. of the carbon sample, accurately graded between 60 and 100 I.M.M. sieves, by 50 c.c. of a solution made by dissolving 10 g. of potassium dichromate in 50 c.c. of syrupy phosphoric acid (*d* 1·75). The solution was stirred by bubbling air through it at constant rate, and the carbon dioxide evolved was absorbed by soda–lime. Under these conditions, the reaction velocity was approximately linear during the initial period.

The coal carbonisations were carried out in a vertical, electrically-heated, silica tube connected at the bottom to a source of oxygen-free nitrogen, purified by passing over heated copper and through a pyrogallol scrubber. From the upper stopper of the furnace tube a silica test-tube was suspended by means of nichrome wire. The upper stopper also carried an exit tube and a silica thermocouple sheath. The air-dried coal (7 g.), graded as above, was placed in the test-tube with the thermocouple sheath embedded in it. The stopper carrying the test-tube, thermocouple, and exit tube was then placed in position, the furnace having previously been raised to the required temperature. After 1 hour's carbonisation in nitrogen, the resulting coke was removed, cooled, graded as before, and a 1 g. sample tested in the wet oxidation apparatus.

The amount of moisture adsorbed by the various samples was determined by measuring the loss in weight which occurred on heating at 105—110° for 1 hour, after several days' exposure to an atmosphere partially saturated with water vapour. The volatile-matter contents of the samples were determined by the standard B.S.I. method (*i.e.*, by determining the loss in weight occurring on heating at 965° ± 15° for 7 minutes in a reducing atmosphere; B.S.S. No. **496**, 1933, p. 11).

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