

CCCXXVIII.—*The Heat of Adsorption of Oxygen on Charcoal. Part II.*

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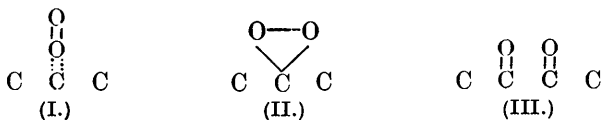
DEBYE and SCHERRER (*Physikal. Z.*, 1917, **18**, 291) concluded from an X-ray examination by the powder method that amorphous carbon was merely graphite in a powder form. This conclusion was criticised by Ruff, Schmidt, and Olbrich (*Z. anorg. Chem.*, 1925, **148**, 313), who are of the opinion that amorphous carbon is a true modification which begins to pass into a para-crystalline variety at 1100°, and that the different forms of amorphous carbon are to be attributed to the admixture of varying proportions of graphite and a para-crystalline form. From their investigation, it would appear that the adsorptive powers of charcoal are due to the amorphous form alone.

The energy content of amorphous carbon is 3 Cals./mol. higher than that of graphite. This difference in energy must be associated with structural differences probably extending throughout the body of the carbon. The most probable structure of amorphous carbon, in view of its mode of formation from cellulose or sugars, is that of an interlocking network of carbon chains, which are the degradation products of the original cellulose molecules. With such a structure, adjacent carbon chains will touch at points irregularly along their length. Where contact occurs between carbon atoms of adjacent chains, presumably something analogous to chemical combination has occurred, but there must exist atoms in the body of the carbon the valency forces of which are not fully saturated by neighbouring atoms. The excess of potential energy of amorphous carbon would be expected to lie in such atoms and in those exposed in the capillary surfaces of the charcoal.

Each of the surface atoms forms part of a chain extending into and rigidly fixed in the body of the carbon. The surface atoms may possess the haphazard distribution of their fellows in the body of the charcoal. Those projecting some distance from the surface are conceivably unsaturated chemically. Birge (*Physical Rev.*, 1926, **28**, 259), from a consideration of results on the heat of vaporisation of carbon and an examination of the molecular spectra of oxygen and the oxides of carbon, concluded that 1 g.-mol. of gaseous carbon contains 141 Cals. more potential energy than carbon in bulk. This value sets the limit for the potential energy of the most active carbon atoms on the surface of charcoal. The potential energy of these atoms will very probably range between 141 Cals. and zero, the former value corresponding with carbon atoms practically in the gaseous state and the latter with atoms almost completely surrounded by neighbouring atoms. The nature of the law of the distribution of energy among the surface atoms is unknown.

The potential energy of the carbon surface should be liberated during chemical changes occurring thereon, *e.g.*, during the adsorption of oxygen. Under the most favourable conditions, the heat of adsorption of this gas should approach a value of the order of 300,000 cal. per g.-mol. of oxygen adsorbed.

There is some justification for assuming that combination between oxygen molecules and carbon atoms on the surface can take place according to definite stoichiometrical relationships. This would be the case if electron sharing occurs between the surface and adsorbed atoms. Also, there is the possibility of physical adsorption, the oxygen being held by subsidiary valency forces on the surface. The following simple structural forms may be present on a carbon surface which has adsorbed oxygen (C C C . . . represents the surface) :



(I) represents the process of physical adsorption of oxygen in which there is no electron transference or sharing between the atoms. The adsorption is, in this case, a reversible process, and the adsorbed oxygen molecules can be recovered unchanged. (II) and (III) are examples of modes of chemical combination. Desorption of oxygen should occur as carbon dioxide in (II) and as carbon monoxide in (III). Other types of complex may exist, but our object is to present as simple a picture as possible.

Our knowledge of these adsorption complexes is based on (a)

the nature of the products obtained on desorption, and (b) measurements of heats of adsorption. The products would appear to depend, not only on the temperature of desorption, but also on factors concerning the adsorption process. The amount of oxygen adsorbed by a given mass of charcoal and the temperature at which adsorption occurs are the main factors involved. At low temperatures and high initial gas pressures, the adsorbed gas can be recovered as oxygen on decreasing the pressure or on raising the temperature (Dewar, *Proc. Roy. Soc.*, 1904, *A*, **74**, 122). This form of adsorbed oxygen is represented by (I). The heat of adsorption is very low, about 3 Cals. per mol. of gas adsorbed. If the gas is admitted at low pressures, *e.g.*, 0.01 mm., and at the ordinary or slightly higher temperature, the adsorbed oxygen can be recovered as oxides of carbon (II and III) on raising the temperature. The heat of adsorption under these conditions is much higher. At room temperature, the maximum heat of adsorption is 70 Cals./g.-mol. (Keyes and Marshall, *J. Amer. Chem. Soc.*, 1927, **49**, 156) and rises rapidly with increase in temperature (Blench and Garner, *J.*, 1924, **125**, 1288). At high pressures and at room temperature, the heat of adsorption is only 4 Cals./mol., and the adsorption complexes may be of all three types, (I), (II), and (III). Rhead and Wheeler (*J.*, 1913, **103**, 471) have shown that the complexes formed at 300° break down into carbon dioxide and monoxide at higher temperatures. Type (II), giving dioxide, would appear to be less stable than (III). The maximum evolution of carbon dioxide occurs at approximately 300—400°, and of carbon monoxide at 600—700° (Rhead and Wheeler, *loc. cit.*). Since both carbon dioxide and monoxide are liberated over a wide range of temperatures,* the forces holding the molecules of the gas on the surface cannot be uniform from molecule to molecule. This is what would be anticipated were the surface adsorbing oxygen truly amorphous.

An investigation continuing the work of Blench and one of us and using a more refined technique has thrown additional light on the nature of the adsorption complexes. The detailed experimental method will be described in a later paper. It will be sufficient to state here that the adsorption was carried out in a vacuum calorimeter of known water equivalent and the rise in temperature measured by means of a thermocouple. The heat of adsorption varies with the initial gas pressure, *i.e.*, with the amount of oxygen adsorbed, in a curious manner. This will be seen by combining the results of McKie and those of Keyes and Marshall (Table I). Although the latter authors measured the heats of adsorption by a

* Only a fraction of the complexes breaks down when the carbon is heated over a range of 50°.

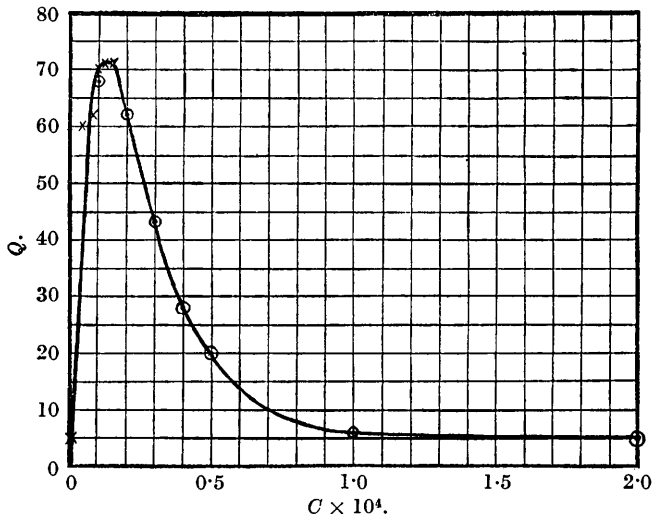
different experimental method (by the ice calorimeter), their results agree very well with those of McKie. Charcoals with practically the same activity must have been used in both series of experiments.

TABLE I.

Heat of adsorption (Cals./mol.).

$C \times 10^4$.	Q per mol. of O_2 at 18° (McKie).	$C \times 10^4$.	Q per mol. of O_2 at 0° (Keyes and Marshall).
0.001 to 0.006	5	0.1	67.9
0.04	60	0.2	61.9
0.08	62	0.3	43.5
0.10	70	0.4	27.9
0.12	71	0.5	20.1
0.15	71	1.0	5.8
		2.0	5.1
		4.0	4.4

FIG. 1.



C represents the number of g.-mols. of oxygen adsorbed per g. of charcoal, and Q is the molar heat of adsorption.* Different charcoals show the same maximum value of Q , although this does not necessarily occur at the same value of C . The results are plotted in Fig. 1. There is a sharp rise in the heat of adsorption up to a maximum value of 70 Cals. and then a slower fall down to 4 Cals. as the density of adsorbed oxygen increases. A similar curve has been obtained by Kistiakowski (*Proc. Nat. Acad. Sci.*, 1927, **13**, 1) for the heat of adsorption of hydrogen on nickel.

* The oxygen admitted is almost completely adsorbed at a surface density of $C = 0$ to $C = 0.1 \times 10^{-4}$.

The internal area of the charcoal used in the above experiments has been determined by measuring the adsorption isotherms of straight-chain alcohols on the charcoal (area = 66 m.² per g.) (Garner, McKie, and Knight, *J. Physical Chem.*, 1927, **31**, 641). At the maximum of Fig. 1, only 1/140 of the carbon atoms are covered with oxygen, so that the range of figures given in Table I refers only to the formation of an incomplete unimolecular film of oxygen molecules on the surface.

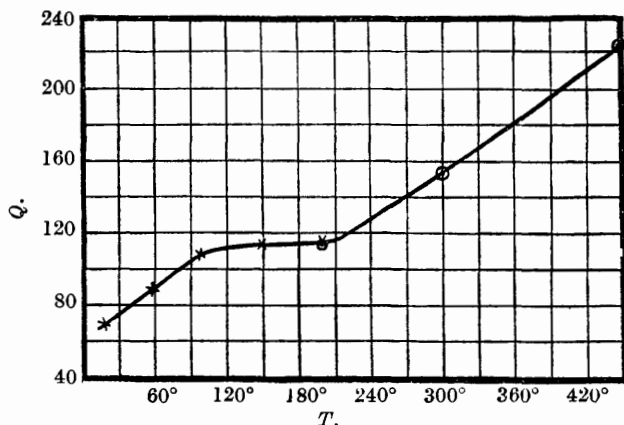
The heat of adsorption varies with the temperature. Values are shown in Table II for $C = 0.1 \times 10^{-4}$. The agreement between

TABLE II.

Relation between heat of adsorption and temperature.

Temperature	18°	57°	100°	150°	200°	300°	450°
Q (McKie)	70	91	108	114	116	—	—
Q (Blench and Garner)	—	—	—	—	115	154	224

FIG. 2.



the values of McKie and those of Blench and Garner at 200° is probably a coincidence, since the latter were not so accurately determined as the former.

Fig. 2 brings out the nature of the rise in Q . This approaches a constant value between 100° and 200° and then rises rapidly. In the interpretation of these results, it is necessary to bear in mind that the accuracy of the values decreases with increase in temperature. Up to 100°, only negligible amounts of carbon dioxide are produced on admitting oxygen to the charcoal, but at higher temperatures this gas is liberated in increasing amounts. At 450°, more than 30% of the oxygen combining with the surface is liberated as dioxide. This makes the deduction of the heat of

adsorption uncertain. Nevertheless, we believe the general trend of the curve to be correct.

The temperature coefficient of the heat of adsorption is too great to be accounted for by changes in the specific heats of the resultants and reactants. It must be due to a change in the type of complex with the temperature. The heat of adsorption approaches a constant value at 100—200°. This suggests that the type of complex which is formed does not undergo much change over this range of temperatures. Below 100°, at least two types must be present, one of which gives place to the other on increase in temperature. This change is nearly complete at 100°. It is highly probable that at this temperature only one structural form is present. This cannot be (I), but is very probably (II). The experiments of Rhead and Wheeler on the decomposition of the complex indicate that this is the case; carbon dioxide is the main product of desorption at 300—400°. If this is so, then the rise in Q above 200° must be ascribed to the formation of (III). If Q were very large for type (III), then a high temperature would be necessary before desorption could be brought about. This is supported by the fact that the maximum evolution of carbon monoxide does not occur until 600—700° is reached.

Although the heat of adsorption obtained between 100° and 200° is believed to be that of type (II), it is not suggested that this heat is other than an average value. Owing to the varying potential energy of the carbon atoms on which the complex is formed, a range of heats of adsorption for type (II) would be expected. This would account for the wide range of temperatures over which the complex is broken down to give carbon dioxide.

Returning to Fig. 1, we are met with greater difficulties in interpretation. The decrease in Q as the amount of gas adsorbed increases is undoubtedly due to the increasing predominance of molecularly adsorbed oxygen (I). The low heat, and the fact that from such charcoals oxygen may be recovered, requires that this be the case. The occurrence of a maximum value and the fall at very low surface concentrations afford an interesting problem for the complete solution of which there are not sufficient data. If it be assumed that the fall is due to the occurrence of physical adsorption at very low pressures, it must also be assumed that the oxygen is very tightly bound to the surface, which occurs very rarely for physical adsorption. At $C = 0.01 \times 10^{-4}$ g. mol./g., only 1 in every 1400 of the surface carbon atoms is covered, and these will be the most unsaturated of the surface atoms. If a physical complex is formed, it may thus be comparatively stable.

An alternative and preferable explanation would be that, at

very low pressures and surface densities, an active form of type (II) is formed which only slowly liberates its internal energy as heat or radiation. The liberation of energy may occur so slowly that we cannot measure it by our methods. In support of this, it may be mentioned that the rate of liberation of heat is slower when $C = 0.04 \times 10^{-4}$ than when $C = 0.1 \times 10^{-4}$. It is probable that an activated form of type (II) would give up its energy if struck by an oxygen molecule, and this may be the explanation of the increased heat of adsorption as the density of the gas above the carbon increases.

Support for this view was found on studying the adsorption of mixtures of oxygen and nitrogen. Nitrogen is adsorbed when admitted together with oxygen in greater amounts than if admitted either to a bare carbon surface or to a surface on which oxygen has been adsorbed. The gas is not, however, held so firmly as either oxygen or nitrogen which has been adsorbed on a bare surface; it evaporates when the pressure is lowered. An unstable carbon, oxygen, and nitrogen complex is formed. The complexes formed when nitrogen is admitted after oxygen are much more stable (compare *Trans. Faraday Soc.*, 1926, **22**, 459).

These results indicate that the adsorbed oxygen molecules are in a chemically active state immediately after formation, and that this activity is lost on standing. They support the view expressed above that the initial portion of the curve in Fig. 1 is due to the formation of a complex of type (II), which has retained a large portion of its heat of formation. A similar explanation can also be given for Kistiakowski's curve (*loc. cit.*).

Summary.

The heat of adsorption of oxygen on charcoal varies with the amount of oxygen adsorbed per g. of charcoal. A maximum value (70 Cals.) was obtained when the number of g.-mols. of oxygen adsorbed per g. of charcoal was 1.5×10^{-5} . The maximum heat of adsorption increases rapidly with increase in temperature, approaching 115 Cals. between 100° and 200° . It rises again from 200° to 450° .

The results have been discussed with regard to the light they throw on the chemical constitution of the C_xO_y complex.

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