CCCCX.—*The Heat of Adsorption of Oxygen on Charcoal.*

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CALORIMETRIC determinations of the heat evolution on adsorption of oxygen by charcoal have been made by Dewar (*Proc. Roy. Soc.*, 1904, *A*, **122**, 1904), Blench and Garner (J., 1924, **125**, 1288), and Keyes and Marshall (*J. Amer. Chem. Soc.*, 1927, **49**, 156). In extending Warburg's work (*Biochem. Z.*, 1924, **145**, 461) on oxidation at charcoal surfaces, Rideal and Wright (J., 1925, **127**, 1347) and Wright (this vol., p. 2323) showed that in a sugar charcoal three different types of surface could be distinguished and their relative areas determined by the method of selective poisoning. The most active area permits autoxidation when the charcoal is shaken with water containing dissolved air or oxygen. The reaction is of zero order, due to the escape of carbon dioxide from the active patches. It is natural to suspect that the portions of the charcoal surface which, according to these observations, are readily autoxidisable would be those on which the energy change, as noted in the calorimetric experiments of Blench and Garner on adsorption of the gas, would likewise be greatest.

Since charcoal is an extremely variable material, and different results are obtained from samples prepared in different ways, it seemed desirable to use several varieties and to attempt to correlate the heats of adsorption of oxygen with other properties of the charcoal. The determination of the heats of adsorption for four different charcoals is now described, together with the rate of autoxidation, the true densities, the apparent bulk densities, the adsorption of methylene-blue at p_H 6·5, and the particle size.

EXPERIMENTAL.

The charcoals employed were: (1) Merck's blood charcoal, purified by digestion with hydrochloric acid and activated by heating in air for ½ hour to dull redness; (2) Griffin's sugar charcoal, reignited and washed; (3) "supra-norite," made from wood dry distilled at 700° and then activated by superheated steam; (4) potash sugar charcoal, prepared by charring lump sugar with 20% of potassium carbonate in a porcelain dish and extracting the mass with hydrochloric acid, and, after prolonged reflux washing with boiling water, activated by ignition in a silver crucible. We are indebted to Dr. C. G. L. Wolf for the last three charcoals.

Determination of the Adsorption of Methylene-blue.—The adsorption isotherms of charcoal for various solutes vary greatly. With iodine or acetic acid, the amount adsorbed is proportional to the bulk concentration over a wide range; but phenol, quinine, and methylene-blue reach adsorption maxima at low concentrations (Honig, *Koll.-Chem. Beih.*, 1926, **22**, 345). Kruyt, Pincussen, and Warburg have offered various objections to the use of methylene-blue, but Paneth and Radu (*Ber.*, 1924, **57**, 1221), from experiments on powdered diamond and charcoal, conclude that the saturation maximum is attained on covering the available surface with a unimolecular layer of the dye. Methylene-blue will, however, give no indication of the extent of the micro-pores owing to the size of the molecule; for example, active coconut charcoal readily adsorbs gases and acetone, but its methylene-blue adsorption is small. The adsorption of many dyes varies with the acidity of the solution, and all determinations were conducted at p_H 6·5. A solution of methylene-blue containing 1 mg. per c.c. was added to 0·1 g. of charcoal (more in the case of sugar charcoal) from a burette until it ceased to be completely decolorised on shaking and keeping for some while. Further quantities of the dye were then added and the residual amounts in the solution were determined colorimetrically with the aid of a Klett biocolorimeter. The results, obtained on the assumptions of Paneth and Radu, that 1 mg. of dye will cover 1 sq. m. of surface, are as follows :

Charcoal.	Areas (sq. m. per g.).	Mean.
(1)	642, 644, 573, 630	622
(2)	8·4 7·5	8·0
(3)	503 546	525
(4)	6·0 5·0	5·5

The ash contents of the dried charcoals, determined by the slow ignition of about 0·5 g. and heating the residue until of constant weight, were :

Charcoal	(1)	(2)	(3)	(4)
Ash content, %	1·00	0·15	9·59	0·37

The densities of the charcoals were determined by opening specimens of charcoal sealed in glass under water after prior exhaustion with a diffusion pump for 5 hours, the charcoals having been heated at 200° to 300° during the process of exhaustion. In such determinations there occurs a " drift " in the values obtained for the densities (Cude and Hulett, *J. Amer. Chem. Soc.*, 1920, **42**, 391), due to the gradual penetration of the liquid into the micro-pores. The values obtained after 15 minutes' immersion are found to differ from the " infinity " value by about one unit in the third decimal place. This period was accordingly adopted as convenient for these experiments. The apparent bulk densities, which gave an indication of the state of aggregation, were determined by weighing the amount of the powders necessary to fill a definite volume, the tubes being tapped to ensure uniformity of packing. The values obtained were reproducible. The charcoals were also examined for possible changes in the apparent bulk densities after the experiments on the adsorption of oxygen had been completed. The results obtained are in the following tables :

		Apparent bulk density	
Charcoal.	True density.	(before).	(after).
(1)	1·37	0·22	0·22
(2)	1·42	0·58	0·58
(3)	2·03	0·14	0·115
(4)	1·43	0·30	0·32

It will be noted that charcoal (3) is relatively unstable, in that the apparent bulk density undergoes a diminution during the process of exhaustion necessary for the determination of the heat of adsorption of oxygen, although the charcoal did not lose weight to any measurable extent during evacuation. This charcoal has a true density of above 2·0, yet its bulk density is least, an indication that the ash of the charcoal probably gives a support to enable the charcoal to exist in a much more porous but unstable state.

The rates of autoxidation of the charcoals were determined at 40° with the aid of a Barcroft differential shaking machine in the manner described by Rideal and Wright (J., 1925, **127**, 1347), and are given for specimens of the charcoal both before and after the determination of the heats of adsorption of oxygen :

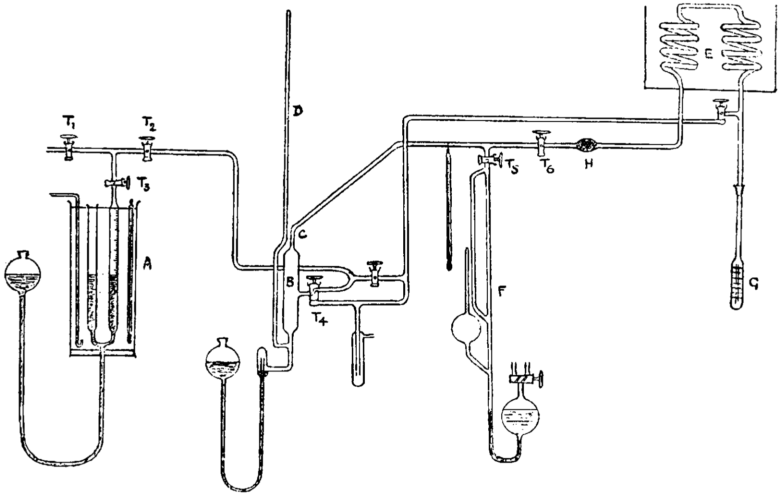
Rate of autoxidation (in mm.^{3} of O_2 at *N.T.P.* per g. per hour at 40°).

Charcoal.	Before adsorption experiments.		Mean.	After adsorption experiments.		Mean.
(1)	232	229	230	242	244	243
(2)	165	159	162	196	208	202
(3)	64·8	72·8	69	218	209	214
(4)	352	364	358	316	318	317

Again it will be noted that charcoal (3) is exceptional, in that the process of prolonged exhaustion necessary for the determination of the heat of adsorption has caused a very considerable increase in the autoxidisable area.

The Determination of Particle Size.—The sizes of the charcoal particles were measured with the microscope and oil-immersion objective, with a scale in the eye-piece. This was standardised by comparison with blood corpuscles (7μ diameter). Charcoals (2), (3), and (4) were fairly homogeneous, but (1) varied considerably, the largest particles being seven or eight times the smallest. For (2), (3), and (4), the maximum variation in size was 3- or 4-fold. Charcoal (1) was made up of particles of very irregular shape, charcoals (2) and (4) were almost cubic or spherical, and in charcoal (3) one-third of its particles consisted of thin rods, with a length of five or six times the thickness. The diameter given below represents for this charcoal an average value of the different dimensions. The mean diameters of the charcoals are as follows (average of measurements on a large number of particles):

FIG. 1.



(1) 8·1μ; (2) 5·8μ; (3) 4·9μ; (4) 5·8μ.

Brownian movements were easily observed in the case of the smallest particles.

Determination of the Adsorption and Heats of Adsorption of Oxygen.—The oxygen was prepared by the electrolysis of a 10% solution of caustic soda, and passed over calcium chloride, solid potash, and phosphoric anhydride; in order to remove any hydrogen present the gas was then passed over palladium–asbestos, and again dried by phosphoric anhydride. The oxygen was introduced into the measuring burette A (Fig. 1), which was enclosed in a water jacket kept at uniform temperature by a fine stream of air bubbles being driven through it.

In an experiment, the taps T_2 and T_3 were kept open, and a measured quantity of the gas was delivered into the vessel B by way of the three-way tap T_4. This was a hollow-barrel tap by which B could be put into communication with either the burette or the high-vacuum pumps (a Langmuir pattern mercury-vapour diffusion pump, backed by a Hyvac pump). The vacuum kept the barrel well pressed down all the time. By raising the level of the mercury in B to the mark C, the gas could be driven over *via* the tap T_6 and the spirals of capillary tubing E (kept in melting ice) into the adsorption vessel G. This was made of Pyrex glass and connected to the rest of the apparatus by a ground joint. Inside G was placed a thin rod of Pyrex with several discs on it, to keep the charcoal from being pressed down too tightly. The possible poisoning of the charcoal by mercury vapour was prevented by a small tube containing gold foil (H in the figure). The pressure of the oxygen was measured on the tube and scale D.

For the measurement of the heat of adsorption, the Bunsen ice calorimeter was used, as described by Schüller and Wartha (*Wied. Ann.*, 1877, **1**, 359). Instead, however, of their method of weighing the mercury which moved along the capillary tube, it was found sufficiently accurate, and much quicker, to measure the distance that the mercury meniscus moved along the tube by means of a scale behind. The inner tube of the calorimeter was about half filled with mercury to ensure good contact with the source of heat placed inside it. The calibration of the instrument was effected by introducing weighed amounts of various metals at known temperatures and with known specific heats, and the movement of the mercury along the scale was observed. After various methods of freezing a sheath of ice round the central tube had been tried, it was found that the most convenient method was to push down the centre an iron rod which had been cooled in liquid air. The mercury caused uniform cooling, and the ice sheath was regular.

Since the water inside the calorimeter is under a slight pressure due to the column of mercury, Lamb and Coolidge (*J. Amer. Chem. Soc.*, 1920, **42**, 1146) put a couple of drops of alcohol in the water of the surrounding vessel to depress its freezing point by the same amount and prevent the gradual movement of the mercury meniscus due to the slow melting of the ice sheath. In these experiments it was found that this effect was altogether masked by the impurity of the ice in the outer jacket, which was at a slightly lower temperature than 0°, and caused a slow freezing inside. This was decreased by first washing the ice in distilled water, but could not be got rid of entirely; this, however, proved to be no disadvantage, for by the method adopted readings could be taken more quickly when there was a slight outward movement of the mercury.

At the beginning of an experiment, a weighed quantity of charcoal was placed in the adsorption vessel, and baked for 2 or 3 days at about 420° until the pressure decreased to about 10^{-5} mm. At the beginning of the evacuation there was always a danger of some of the charcoal being carried away owing to the rapidity of evolution of gas. To prevent this a small wad of cotton wool was placed in the tube leading out of the adsorption vessel.

When the pressure was sufficiently low, the tap T_5 was closed, and the McLeod gauge shut off from the rest of the apparatus. The ice calorimeter was then placed under the adsorption vessel and raised into position. After equilibrium had been reached (about 2 hours), a small amount of gas was transferred from the burette A into B, and then driven into the vessel C. The pressure of the oxygen, as measured on the scale D, gradually decreased as more of the gas was adsorbed, and at the end of about ¼ hour had reached its final value. More gas was then transferred from the burette, and the procedure repeated. At each reading of the pressure or volume, the temperature of the air in the neighbourhood of the apparatus and that of the water jacket round the burette were observed.

The volume of the adsorption vessel and the tubes leading to it, as far as the mark C, had previously been determined by letting in various known amounts of gas and measuring the pressure. In an actual adsorption experiment, part of the volume of the system is at room temperature, and part at 0°. The volume of the part at room temperature was found by measuring the lengths and internal diameters of the various tubes that made it up, and by subtracting this from the total volume, the volume of the part at 0° was found. The relative amounts of these two volumes need not be known so accurately as the total volume, as the error due to this is not so great.

The amount of gas adsorbed was determined as follows.

Let v_1 = volume of system at room temperature; v_2 = volume of system at 0° (allowance must be made here for the volume actually occupied by the charcoal); P = atmospheric pressure; p = pressure of gas in the system; t = room temperature; T = temperature of burette; and V = volume of gas from burette. Then if the volume of V corrected to *N.T.P.* is V',

$$V' = 273VP/760(273 + T).$$

If the volume of gas which fills v_1 becomes v_1' when reduced to *N.T.P.*, then

$$v_1' = 273v_1p/760(273 + t);$$

v_2' similarly defined would then be given by $v_2' = pv_2/760$, and the amount of gas adsorbed (in c.c. at *N.T.P.*) would be $V' - (v_1' + v_2')$. From this the amount adsorbed per g. is easily found. The results obtained with the various charcoals are given graphically, the amount of oxygen adsorbed being plotted against the pressure.

With the calorimeter in position scale readings were taken at frequent intervals and plotted against time on as large a scale as possible. In the intervals between the liberations of heat, parallel straight lines were obtained, but when the gas was let in there was a resulting inflexion in the curve, which again became straight when equilibrium was reached. The distance between the lines, measured parallel to the axis of scale readings, was proportional to the heat evolved. With the capillary tube used, the sensitivity of the instrument was about 0·5 cal. per mm. of the scale. The sensitivity of the calorimeter depends, of course, on the diameter of the capillary tube, but it is not convenient to use capillary tubes narrower than this, as the mercury sticks and makes accurate reading difficult.

By this means the evolution of heat was found for each small addition of gas, and after summing these, a curve was plotted for the total amount of heat liberated against the total amount of gas adsorbed at different pressures (integral heat of adsorption). The slope of the tangent to the curve at any point gave the differential heat of adsorption in cals. per c.c. or cals. per g.-mol. according to the scale used. These values were then plotted against the amount of gas adsorbed.

Results.

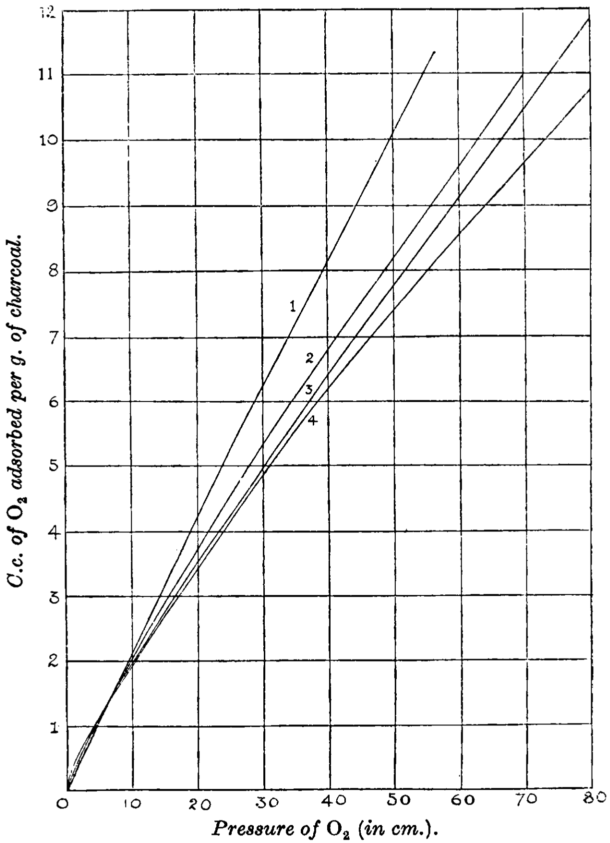
Table I is an example of the experimental results [for the charcoal (1)]. For the other charcoals similar results were obtained, but these are only shown graphically.

TABLE I.

Expt.	Press. of O_2 (cm.).	C.c. O_2 adsorbed per g.	Sum of differential heats (cals. per g.).	Expt.	Press. of O_2 (cm.).	C.c. O_2 adsorbed per g.	Sum of differential heats (cals. per g.).
(1) 1	11·20	2·35	0·96	(1) 3	10·85	2·38	1·20
	26·10	5·28	1·53		23·85	5·06	1·66
	40·75	8·05	2·30		35·47	7·37	2·14
(1) 2	13·20	2·90	1·62		50·80	10·37	2·64
	20·50	4·38	1·97		62·70	12·42	3·11
	38·48	8·02	2·74	(1) 4	1·52	0·28	0·48
	49·21	10·05	3·30		3·15	0·65	0·71
	71·71	14·08	4·03		8·00	1·77	1·01
(1) 3	1·00	0·21	0·38		20·53	4·54	1·39
	3·30	0·72	0·76		55·40	11·22	2·54
	5·87	1·38	0·92		70·30	13·82	3·07

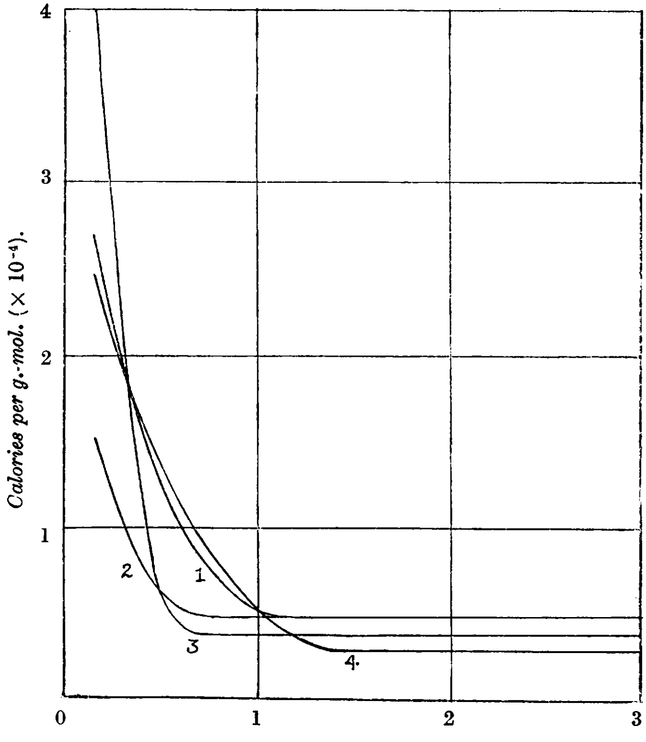
The amounts of oxygen adsorbed at different pressures are shown on the adsorption isotherms (Fig. 2). For any particular charcoal, the figures found in the different runs fall very closely on the same curve. There is not much difference in the curves for the different charcoals, (2), (3), and (4) being almost identical, and (1) slightly greater. The isotherms, although not quite straight lines, are nevertheless very far from the shape to be expected if the adsorption maximum were almost reached. They are very nearly linear at the beginning of the curve, when the amount adsorbed is almost directly proportional to the pressure. Just by the origin, however, there is a slight divergence from this, especially noticeable for the charcoal (4). The curve, which is nearly straight down to about 4 cm., bends downwards and becomes slightly concave to the pressure axis; *i.e.*, at low pressures the charcoal adsorbs rather more oxygen for a given pressure increase than at higher concentrations. This effect occurs also with (2) and (3) although to a less extent.

Fig. 2.



More marked differences in behaviour between the charcoals are found when the heat of adsorption of oxygen (in cals. per g.-mol.; mean of several experiments) is plotted against the amount adsorbed, Fig. 3. For one charcoal, the agreement in this case between different runs is not nearly so good as for the adsorption isotherm. This is not due to inaccuracies of measurement, for the divergencies obtained are much greater than the possible error of the ice calorimeter. The charcoal surface must have been altered in some way during the out-gassing between runs. As far as possible, the same temperature was used in all cases, but owing to difficulties of control, an error of 10° in the regulation was not impossible; moreover, owing to various circumstances, the out-gassing was continued for different times (1, 2, or 3 days).

FIG. 3.



C.c. adsorbed per g. of charcoal.

The first noteworthy point about the heat evolution curves is the initial steep part, owing to the relatively high heat of adsorption for the first amount of oxygen adsorbed. On account of the small capacity of the calorimeter system it was found impracticable to work with more than 1·5 g. of charcoal; in addition, the sensitivity was such that accurate measurements both of the amounts of oxygen adsorbed and of the corresponding thermal evolution could not be conducted on less than 0·15 c.c. adsorbed per g. With these quantities, the ascending portions of the Q,x curve noted by Garner would not be obtained, but the relatively high heats of adsorption for the initial steep portions of the curve could be accurately determined. In the graphs, the straight portions of the curve indicate uniformity of properties and a constant heat of adsorption, but the portions near the origin correspond to the areas of the charcoal more active in adsorption. From a determination of the area covered by this amount of oxygen, the area of the active patches can readily be found. The volumes of oxygen adsorbed with an increased heat evolution are approximately as follows:

Charcoal	(1)	(2)	(3)	(4)
C.c. strongly adsorbed (per g. at *N.T.P.*)	1·0	0·6	0·6	1·3

Taking the radius of the oxygen molecule as 1·81 Å. (Jeans, "Dynamical Theory of Gases"), we obtain for the respective areas

(1) 2·78 m.^{2}; (2) 1·67 m.^{2}; (3) 1·67 m.^{2}; (4) 3·62 m.^{2}.

These areas vary in the same order as do the rates of autoxidation of the charcoals. Neglecting charcoal (3), which we have noted as being extremely variable in nature and possessing a very high initial heat of adsorption for oxygen, we obtain the following ratios between the areas of the active portions and the rates of autoxidation.

$$(1)\ 2{\cdot}78/230 = 0{\cdot}0121;\quad (2)\ 1{\cdot}67/162 = 0{\cdot}0103;$$
$$(4)\ 3{\cdot}62/358 = 0{\cdot}0101.$$

This agreement is as satisfactory as could be expected in view of the inaccuracies in estimating the areas of the patches with high heats of adsorption. A further comparison may be made with the data on selective poisoning furnished by the experiments of Rideal and Wright (*loc. cit.*). In their experiments, it was found that poisoning of the autoxidation of a charcoal, which consumed oxygen at the rate of 0·013 mm.^{3} per mg. per hour at 40°, was effected on adsorption of $2{\cdot}38 \times 10^{15}$ molecules of amyl alcohol per mg.

With this value, and since poisoning of autoxidation appears to be a linear function of the amount adsorbed, it is possible to calculate the number of molecules of amyl alcohol which would be necessary to poison these much more active charcoals, and to compare these values, derived from entirely different charcoals and by a different method, with the quantities of oxygen adsorbed on the active areas. These data are in the following table:

Charcoal.	Rate of autoxidation (mm.^{3} per g. per hr. at 40°).	No. molecules amyl alcohol ($\times 10^{-19}$) per g. required to poison.	C.c. of O_2 adsorbed per g. with high heat of adsorption.	Equiv. no. of molecules ($\times 10^{-19}$) adsorbed per g.	Ratio, $\frac{\text{Col. 3}}{\text{Col. 5}}$.
(1)	230	4·22	1·0	2·70	1·56
(2)	162	2·96	0·6	1·62	1·83
(3)	67	1·22	0·6	1·62	0·75
(4)	358	6·56	1·3	3·52	1·86

On comparison of the data in cols. 3 and 5 for the charcoals (1), (2), and (4), it is clear that the method of poisoning with amyl alcohol and the thermal method for oxygen adsorption yield results for the extent of the autoxidisable areas of charcoals in close agreement with one another. It cannot, of course, be definitely stated that all the oxygen molecules adsorbed with a heat evolution in excess of the normal relate to the autoxidisable portion, or that the ratios in col. 6 bear any relationship to the relative covering powers of amyl alcohol and oxygen molecules on the charcoal surfaces, for there is no reason to suppose that the selectiveness of the adsorptions on the active portions of the charcoal surfaces is identical for each material. It is interesting to note that these ratios are consistent for the three stable charcoals when it is assumed that all the oxygen adsorbed with a high heat evolution is autoxidisable; if the assumption is restricted to the quantity of oxygen adsorbed with heat evolutions exceeding 10,000 (or 20,000) cals. per g.-mol., then the ratio between this quantity and the rate of autoxidation shows rapidly increasing discrepancies between the different charcoals.

Finally, Keyes and Marshall supposed that the high initial heat corresponded to the first unimolecular layer, and that the lower subsequent heats were due to the building up of thicker films of adsorbed oxygen, but as a result of our work their view seems improbable for the following reasons : The fact that the adsorption isotherm is nearly a straight line means that the charcoal is not nearly saturated; and also, to take the case of charcoal (1) which is most adsorbent, even at atmospheric pressure the oxygen only covers 1/50 of the methylene-blue area, and, on account of the large size of the molecule of the dye, this is a considerable under-estimate of the total area available for the oxygen.

Summary.

1. Experiments have been conducted on four different types of charcoal and the following properties investigated : the adsorption of oxygen and the heat of adsorption, the rate of autoxidation, the area of methylene-blue adsorption, the ash content, the true and the apparent bulk densities, and the particle size.

2. The high initial heats of adsorption have been determined and

the areas of the corresponding active patches have been found to be proportional to the rates of autoxidation of the charcoals.

3. The covering power of oxygen has been compared with that of amyl alcohol and shown to be of the same order and to have a constant ratio for all charcoals.

4. In the case of a charcoal with a high ash content, an instability of the carbon surface and a very high initial heat of adsorption for oxygen were found.

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