# **72.** *Active Charcoal. Part II. The Constitution of the Surface and the Activated Adsorption of Water.*

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IN recent years adsorption by active charcoal has been extensively investigated, and from the results of adsorption measurements, various theories have been advanced to account for the mechanism of adsorption and for the possible surface constitution of active charcoal. It is, however, unfortunate that no precise definition has been formulated to characterise " active charcoal," and this has resulted in the rather loose acceptance of the term as applying to any charcoal which has undergone all manner of treatments subsequent to its production by some form of carbonisation from diverse organic substances. To provide some standard of comparison in adsorption measurements, it has been emphasised recently that a more rigid control of experimental material is necessary, and it is clearly desirable, in view of its extensive use, to limit the term " charcoal " to some clearly defined homogeneous substance. For these reasons it is suggested to restrict the name to those completely carbonised substances which contain a preponderating proportion of the element carbon and comparatively small proportions of the elements oxygen and hydrogen; the admission of the latter is permissible, since water is invariably present owing to condensation of the vapour from the atmosphere. This involves no serious restriction for investigations in surface chemistry, since there are abundant supplies of organic materials which can furnish the charcoal and contain only the permissible elements. That foreign impurities considerably influence the mechanism of adsorption is well known; *e.g.*, Burstein and Frumkin (*Trans. Faraday Soc.*, 1933, **28**, 273) have shown the marked increase in the adsorption of hydrogen by active charcoal caused by the addition of 0·2% of platinum, and this is a small quantity compared with the inorganic ash content of many charcoals which are extensively employed. Polanyi (*ibid.*, p. 317) has also pointed out that ions on the surface of adsorbents such as charcoal, silica gel, oxides, etc., can act as strong electrical centres for the adsorption of molecules of large dipole moment.

Schilov and his collaborators (*Z. physikal. Chem.*, 1930, *A*, **148**, 233; **149**, 211) have attempted to classify active charcoals with particular reference to their adsorbing capacity for inorganic acids and bases, and conclude that, under given conditions of temperature and pressure, surface oxides are produced which are of an acid, basic, or amphoteric character and possess, therefore, correspondingly different properties. They claim to have established the existence of three clearly defined surface oxides which they call A, B, and C and have even given a tentative formulation of their structures. Their conclusions have received a large measure of support from other investigators and have been widely accepted. Frumkin and collaborators (*ibid.*, 1931, **157**, 442; 1929, **141**, 141) prefer to regard the mechanism of adsorption as governed by the electrical conditions of the surface and consider that charcoal behaves as a gas electrode and can function as an oxygen or hydrogen electrode, according to whether the solution with which it is in contact contains oxygen or hydrogen; they do not, however, exclude the possible existence of surface oxides. The hypothesis of some form of carbon–oxygen union on the surface of charcoal is not new, and Rhead and Wheeler (J., 1913, **103**, 461) suggested the existence of a complex $C_xO_y$. Lowry and Hullett (*J. Amer. Chem. Soc.*, 1920, **42**, 1408) have postulated the existence of a " stable solid oxide " of carbon on charcoal at ordinary temperatures, which decomposes on heating into carbon monoxide and dioxide, and quote evidence for the existence of mellitic anhydride, $C_{12}O_9$, and of $C_{16}O_6$, and also refer to their own work on a colloidal oxide $C_3O$. Kobe (*J. Chem. Educ.*, 1931, **8**, 232) has postulated the existence of four oxides of carbon (other than the two simple oxides), *e.g.*, $C_3O_2$, $C_5O_5$, $C_6O_6$.

Since active charcoals have large surface areas and can therefore adsorb large quantities of gas, it might be expected that information would be obtained from the many published analyses of charcoals as to their oxygen contents. Unfortunately, with only one or two exceptions (see p. 299), the charcoals investigated have contained appreciable proportions of other elements (inorganic ash, nitrogen, etc.) and so the results are difficult to interpret. In these investigations the moisture content has generally been obtained by heating in air, or some inert gas such as nitrogen, to arbitrarily selected temperatures, usually below 300°; the water obtained in the subsequent combustion with oxygen has been regarded as originating from hydrogen, and the oxygen obtained by difference.

In Part I of this series (J., 1932, 1864) the adsorption isotherms of six organic acids with four ash-free activated charcoals were described. The charcoal was obtained by carbonisation of A.R. saccharose, and four preparations were activated by different methods (*ibid.*). All the isotherms conformed to Langmuir's adsorption equation (*J. Amer. Chem. Soc.*, 1918, **40**, 1360) which can be written in the form $1/\Gamma = k/C + 1/\Gamma_{\text{max.}}$, where $\Gamma$ is the number of solute molecules adsorbed at the equilibrium concentration $C$ in the solution, $\Gamma_{\text{max.}}$ the maximum number adsorbed in a unimolecular layer, and $k$ the equilibrium constant. The unexpected result was obtained that $k$ was the same for each acid for the different charcoals, and it was therefore concluded that, although the charcoals had unequal surface areas, since $\Gamma_{\text{max.}}$ differed, yet the surfaces must be identical in nature, despite their varied treatments, for any alteration in their character would be reflected in variations in the constant $k$. These results have led the author to question the validity of the hypothesis of surface oxides, since it would appear that these would manifestly be affected by the varying treatments which the charcoals have undergone and would, in turn, affect the magnitudes of the equilibrium constants.

Large values were found for the available surface areas (*loc. cit.*), and it was shown that about 10—20% of the carbon atoms of the charcoal must lie in the surface available for adsorption. Since this is so, it is clear that for 1 g. of charcoal a unimolecular layer of oxide would contain about 0·15—0·25 g. of oxygen, on the assumption of an equivalence of oxygen to surface carbon. A large quantity such as this should be easily estimated in an analysis, and it was accordingly decided to analyse the charcoals. The analyses were confined to charcoals A, B, and $C_2$, since none of $C_1$ was available, but, since B had received similar treatment, $C_1$ would doubtless be of similar character.

The results obtained are surprising and provide unexpected information on the much-discussed phenomenon of " activated adsorption."

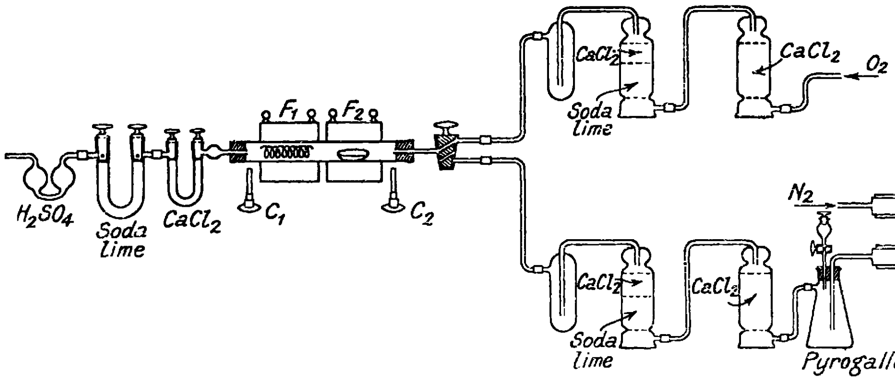
## EXPERIMENTAL.

A preliminary combustion of charcoal A with oxygen in a quartz tube heated to 1000° in an electric furnace showed that the charcoal was converted into approximately equivalent proportions of carbon monoxide and dioxide, in agreement with the observations of Meyer (*Z. physikal. Chem.*, *B*, **1932**, **17**, 385). To eliminate the necessity of estimating the monoxide as well as the dioxide, the former was converted into the latter by oxygen with platinised asbestos, which had been heated in the tube for several days in a stream of oxygen until free from condensable gases. In a trial attempt, 0·4150 g. of charcoal, previously heated for 48 hours at 110° in an electric oven, yielded 103·9% of its weight of carbon dioxide and water.

For more detailed analyses, the apparatus shown diagrammatically in Fig. 1 was used. Alkaline pyrogallol served both to detect and to eliminate traces of oxygen in the nitrogen stream not removed by the copper gauze (maintained at dull red heat); it was obtained colourless by dissolving the acid in water, saturating the solution with nitrogen, and running it into aqueous caustic soda (also saturated with nitrogen) from a dropping funnel in an atmosphere of nitrogen, and it did not darken very much throughout the course of many runs. The traps immersed in liquid air were used as a precaution to remove condensable vapours, but there did not appear to be any.

Blank runs showed that platinised asbestos, when exposed to the atmosphere, absorbs large quantities of moisture, and the quartz combustion tube also gave up appreciable quantities of water; before each experiment, therefore, the asbestos and the quartz tube, with calcium chloride and soda–lime absorption tubes attached to the exit end, were heated in a stream of nitrogen to 1000° and then cooled in a stream of the purified nitrogen which filled the tube at atmospheric pressure before each experiment was commenced; modifications in detail are described for each analysis later. The absorption tubes for water contained A.R. calcium chloride, and those for carbon dioxide were filled with soda–lime and calcium chloride. In the runs requiring nitrogen as the streaming gas, the absorption tubes were filled first with nitrogen before weighing; only two calcium chloride and two soda–lime tubes were used (one of each at a time) since in this way the successive increments of water and carbon dioxide evolved at different temperatures from the charcoals were determined under the same conditions. A standardised procedure for cooling and weighing was adhered to throughout. The charcoals A, B, and $C_2$ were kept in a desiccator over calcium chloride and allowed to come to equilibrium in the silica boat in the balance before weighing. A small pulsimeter containing sulphuric acid served to control the gas stream and to prevent the pressure in the absorption tubes from rising above atmospheric.

FIG. 1.



The platinised asbestos catalyst was kept at a constant temperature of 800° by furnace $F_1$ during each experiment, and the temperature of the charcoal under investigation could be varied by the resistance system connected with furnace $F_2$.

The time elapsing between the disconnection of one absorption train and the attachment of another in the nitrogen runs was only a matter of a few seconds, so no appreciable losses of evolved gases from the charcoal were to be expected.

The compressed-air jets $C_1$ and $C_2$ were used to prevent the rubber stoppers from charring, and $C_2$ further served to condense any sudden rushes of water evolved from the charcoal; the temperatures at which condensation occurred could be observed on the platinum–platinum-rhodium thermocouple register. It was found that a minimum of about 5 mg. of water was required to produce a readily observable film of water on the exit end of the quartz combustion tube.

### *Results.*

*Charcoal A.—Analysis* 1. Before the experiment commenced the platinised asbestos and quartz tube were heated for 4 hours at 1000° in a stream of nitrogen and the tube was allowed to cool in cold nitrogen before insertion of the charcoal; then the catalyst was heated for 1 hour at 800° before the charcoal was heated.

| Streaming nitrogen. | | Combustion in oxygen at 800°. | |
|---|---|---|---|
| Temp. of charcoal. | $H_2O$ evolved, g. | Carbon as $CO_2$, g. | $H_2O$, g. |
| Up to 200° | 0·0100 | 0·4095 | 0·0308 |
| ,, 500 | 0·0038 | | |
| ,, 700 | 0·0292 | C + total $H_2O$ = | 0·5001 g. |
| ,, 900 | 0·0168 | Charcoal taken = | 0·4926 g. |
| | Total 0·0598 | Diff. = | +0·0075 g. |

*Analysis* 2. The experimental conditions were the same as in the previous analysis. It had been observed that the water was not evolved continuously but in rushes, and condensed for an appreciable time on the exit end of the combustion tube before being carried off in the nitrogen stream and collected in the absorption tube. The temperatures at which these rushes occurred were observed and no water was detected until a certain critical temperature was reached. These temperatures are recorded below. To prevent any appreciable lag in the observation of the rush temperatures, the temperature of the charcoal was raised very slowly while the rate of flow of nitrogen was made very fast. The accuracy of the temperature readings is ± 5°.

| Streaming nitrogen. | | | Combustion in $O_2$ at 800°. | |
|---|---|---|---|---|
| Temp. of charcoal. | $H_2O$ evolved, g. | Critical temp. for condensation of $H_2O$. | Carbon as $CO_2$, g. | $H_2O$, g. |
| Up to 250° | 0·0130 | Room temp. | 0·4260 | 0·0154 |
| ,, 500 | 0·0027 | | | |
| ,, 700 | 0·0312 | 580°<br>640 | C + total $H_2O$ = | 0·5168 g. |
| ,, 850 | 0·0196 | 780 | Charcoal taken = | 0·5093 g. |
| ,, 950 | 0·0099 | 940 | | |
| | Total 0·0754 | | Diff. = | +0·0075 g. |

Since water is evolved in appreciable quantity in the nitrogen stream at temperatures up to 950° it is possible that the water obtained in the complete combustion (in oxygen) is tightly bound water which would have come off if it had been possible to heat to temperatures above 1000°, but it was not possible to test this hypothesis in the apparatus employed; it is, however, supported by the close agreement between total carbon and water and the quantity of charcoal used.

The experimental conditions were improved in the subsequent analyses and still closer agreement was obtained.

*Analysis* 3. The catalyst and combustion tube were baked for 8 hours at 1000° in a stream of purified nitrogen. Before inserting the silica boat containing the charcoal, the section of the quartz tube containing the catalyst was heated to 1000° for 2 hours and kept at this temperature, and the charcoal was inserted quickly into the cold part of the tube.

| Streaming nitrogen. | | | Combustion in $O_2$ at 800°. | |
|---|---|---|---|---|
| Temp. of charcoal. | $H_2O$ evolved, g. | Critical temp. for condensation of $H_2O$. | Carbon as $CO_2$, g. | $H_2O$, g. |
| Up to 250° | 0·0147 | Room temp. | 0·3778 | 0·0120 |
| ,, 500 | 0·0034 | | | |
| ,, 600 | 0·0222 | 580° | C + total $H_2O$ = | 0·4686 g. |
| ,, 700 | 0·0216 | 640 | Charcoal taken = | 0·4665 g. |
| ,, 850 | 0·0125 | 780 | Diff. = | +0·0021 g. |
| ,, 950 | 0·0039 | — | | |
| | Total 0·0783 | | | |

*Analysis* 4. Conditions as in 3.

| | | | | |
|---|---|---|---|---|
| Up to 250 | 0·0169 | Room temp. | 0·4107 | 0·0122 |
| ,, 500 | 0·0062 | | | |
| ,, 600 | 0·0177 | 575 | C + total $H_2O$ = | 0·4997 g. |
| ,, 700 | 0·0206 | 650 | Charcoal taken = | 0·4990 g. |
| ,, 850 | 0·0098 | 780 | Diff. = | +0·0007 g. |
| ,, 950 | 0·0058 | 940 | | |
| | Total 0·0770 | | | |

*Analysis* 5. The tube and catalyst were baked for 8 hours at 1000° in a stream of purified nitrogen and then heated for 24 hours at 600° in a vacuum. Nitrogen was then admitted until the pressure reached atmospheric and was then permitted to stream through, and the furnace $F_2$ turned off; when the part of the combustion tube in $F_2$ attained room temperature, as in the previous cases, the catalyst (furnace $F_1$) was heated for 2 hours at 1000° before inserting the charcoal. The agreement obtained was of the same order as in Analyses 3 and 4, and it seems that the charcoal consists exclusively of carbon and water.

| | | | | |
|---|---|---|---|---|
| Up to 250° | 0·0138 | Room temp. | 0·4090 | 0·0120 |
| ,, 500 | 0·0037 | | | |
| ,, 600 | 0·0170 | 575° | C + total $H_2O$ = | 0·4921 g. |
| ,, 700 | 0·0194 | 650 | Charcoal taken = | 0·4940 g. |
| ,, 850 | 0·0121 | 780 | Diff. = | −0·0019 g. |
| ,, 950 | 0·0051 | 940 | | |
| | Total 0·0711 | | | |

*Analysis* 6. A complete combustion without preliminary treatment with nitrogen confirmed this, and satisfactory agreement was obtained. The subsequent analyses were carried out with the preliminary treatment as in Analysis 3.

Combustion with oxygen : C = 0·2454 g.; $H_2O$ = 0·0507 g.; total = 0·2961 g. Charcoal taken = 0·2949 g. Diff. = + 0·0012 g.

*Charcoal B.—Analysis* 7. In view of the results obtained it was of interest to find the effects (if any) of extensive grinding on the surface layer of the charcoal. The results of an analysis on a small sample of charcoal A which had been ground for 120 hours (Charcoal B) were as follows :—

| Streaming nitrogen. | | | Combustion in $O_2$ at 800°. | |
|---|---|---|---|---|
| Temp. of charcoal. | $H_2O$ evolved, g. | Critical temp. for condensation of $H_2O$. | Carbon as $CO_2$, g. | $H_2O$, g. |
| Up to 250° | 0·0139 | Room temp. | 0·3296 | 0·0086 |
| ,, 500 | 0·0051 | | | |
| ,, 600 | 0·0198 | 575° | C + total $H_2O$ = | 0·4235 g. |
| ,, 700 | 0·0212 | 650 | Charcoal taken = | 0·4197 g. |
| ,, 850 | 0·0103 | 780 | Diff. = | +0·0038 g. |
| ,, 950 | 0·0050 | — | | |
| | Total 0·0753 | | | |

The results obtained indicate that prolonged grinding has not significantly altered the surface properties of the charcoal, in agreement with the unaltered adsorption constants found in Part I.

*Charcoal $C_2$.—Analysis* 8. An analysis of a sample of charcoal A ground for 72 hours and then degassed and reactivated at 500° (Charcoal $C_2$) was then performed :

| | | | | |
|---|---|---|---|---|
| Up to 250° | 0·0134 | Room temp. | 0·2550 | 0·0073 |
| ,, 500 | 0·0036 | | | |
| ,, 600 | 0·0090 | Not obs. | C + total $H_2O$ = | 0·3243 g. |
| ,, 700 | 0·0143 | 650° | Charcoal taken = | 0·3215 g. |
| ,, 850 | 0·0151 | 775 | Diff. = | +0·0028 g. |
| ,, 950 | 0·0068 | 945 | | |
| | Total 0·0622 | | | |

The only effect of degassing and reactivation on the ground charcoal appears to be a slight displacement of water such that larger quantities are evolved at the higher temperatures at the expense of the water which, in the previous examples, came off at lower temperatures. It is significant, however, that the same critical temperatures were required before the sudden evolutions of water were observed. The results obtained are in conformity with the constancy of the adsorption constants found for charcoals A, B, and $C_2$ in Part I.

In the various analyses, the time intervals between the temperature rises during the streaming nitrogen experiments were varied between 20 minutes and 2 hours, to determine whether prolonged heating would result in any increase in the amount of water evolved. There was, however, no evidence that the duration of heating had any effect on the quantity of water driven off at any given temperature.

Small and variable quantities of carbon dioxide were given off during the heating of the charcoals in the nitrogen stream at the lower temperatures in the various analyses. These have been estimated as carbon and added to the total carbon; this procedure is believed to be justified since the additional gas is not thought to be due to sorbed carbon dioxide. It was impossible entirely to exclude oxygen from the combustion tube since this had to be opened to insert the charcoal and also to replace the absorption tubes. Further, the charcoal was stored and weighed in air, and hence the capillaries contained oxygen and some of this would probably react with the charcoal to give carbon dioxide on heating. It is significant that the ground charcoals B and $C_2$, the capillaries of which would be crushed or filled up to some extent (Part I), gave off negligible amounts of carbon dioxide. It was found that if the nitrogen was passed over the charcoal at room temperature for a long time at the commencement of the experiments, the carbon dioxide given off on raising the temperature was reduced to very small proportions.

The results obtained indicate that the charcoals A, B, and $C_2$ are composed of carbon and water, most of the latter being strongly held by the charcoal surfaces, and since at the highest temperatures employed (950°), appreciable quantities of water are still evolved, it is reasonable to assume that the relatively small amounts of water obtained in the combustions with oxygen would also be given off in the nitrogen stream if sufficiently high temperatures could be attained. In any event it is clear that a great preponderance of the water can be accounted for as adsorbed water since it came off in the nitrogen stream, *i.e.*, under conditions in which there could be no production of water due to combustion of surface hydrocarbons or adsorbed or occluded hydrogen. The results obtained led to the conclusion that a charcoal degassed and activated at 950° would exhibit the characteristics of charcoals A, B, and $C_2$, after these had been heated in a nitrogen stream to 950°, for, since the water found on these charcoals between 500° and 950° is stripped off at 950°, a charcoal initially activated at 950° would possess no bound water which could be driven off below 950°. To test this conclusion, 2·4147 g. of inactive sugar charcoal (the source of A, B, and $C_2$) were degassed and activated at 950° in the manner described previously (J., **1932**, 613). The degassing was carried out for 4 hours with a Cenco Hyvac pump (0·001 mm.); large quantities of non-condensable gases and water vapour were evolved in sudden rushes as the temperature was slowly raised to 950°. The charcoal was then activated with 2·4 litres of purified air, 1·6242 g. of active material (charcoal D) being obtained, which, on standing in the open for 24 hours, increased in weight by 0·0449 g.

*Charcoal D.—Analysis* 9.

| Streaming nitrogen. | | | Combustion in $O_2$ at 800°. | |
|---|---|---|---|---|
| Temp. of charcoal. | $H_2O$ evolved, g. | Critical temp. for condensation of $H_2O$. | Carbon, g. | $H_2O$, g. |
| Up to 250° | 0·0135 | Room temp. | 0·4036 | 0·0101 |
| ,, 500 | 0·0004 | | | |
| ,, 600 | 0·0003 | | | |
| ,, 700 | 0·0000 | | | |
| ,, 850 | 0·0012 | | | |
| ,, 970 | 0·0031 | | | |
| | Total 0·0185 | | | |

C + total $H_2O$ = 0·4322 g.
Charcoal taken = 0·4310 g.
Diff. = +0·0012 g.

The water given off up to 250° is approximately equal to the proportional increase in weight on standing in air, showing that the increase is due to adsorption of water vapour from the atmosphere at room temperature; that given off from 250° to 970° is exceedingly small, and that obtained in the combustion in oxygen is about the same as that given off by the charcoals A, B, and $C_2$ under the same conditions. Hence, it is evident that charcoal D resembles the former charcoals after these have been heated in nitrogen to 950°.

## DISCUSSION.

The exponents of the theory that the processes of adsorption by active charcoal are determined by the existence of surface oxides suggest that these oxides are formed by the oxidation of the carbon atoms at the charcoal surface and are of varied character since charcoals activated (*i.e.*, oxidised) by oxygen or air possess the property of adsorbing inorganic acids or bases according to the temperature of activation. Schilov and his co-workers maintain that an acid oxide (oxide B), which confers on charcoal the property of adsorbing alkali hydroxides, is produced by activation in the temperature range 300—800° with 450—500° as the *optimum* temperature conditions. Kruyt and de Kadt (*Kolloid Z.*, 1929, **47**, 44), who have produced charcoals activated within the same temperature range, and which have this capacity for adsorbing alkali bases, suggest that the charcoal surface is composed of an intermediate product of mellitic acid. All the investigators mentioned find that charcoals activated or ignited at 900—1000° lose their capacity for adsorbing alkalis, but can adsorb mineral acids. Similar results have also been reported by Bartell and Miller (*J. Amer. Chem. Soc.*, 1922, **44**, 1866), who also found that the " acid oxide " charcoals adsorbed the strong organic bases tetramethyl- and tetraethyl-ammonium hydroxides, but not the weak inorganic base ammonia. Quite recently, Kolthoff (*J. Amer. Chem. Soc.*, 1932, **54**, 4473) has published the results of an intensive study on charcoals from different sources activated at 400° and at 950—1000°, and has supported the conclusions of Kruyt and de Kadt.

In this investigation, the charcoals examined (A, B, and $C_2$) were activated at 500°, which is a favourable temperature for the production of these " acidic oxide " charcoals. In every case, however, the analyses show clearly that there is no oxygen present on the charcoal which can confirm the hypothesis of the existence of an acidic oxide, but it has been shown that the charcoals are composed exclusively (within the experimental error) of carbon and water, the latter being evolved on heating at definite temperatures. A charcoal activated at 950° (charcoal D) is stripped of this water layer found on the charcoals activated at 500°. It would appear, therefore, that the capacity of adsorbing alkali hydroxides possessed by charcoals activated at 500° and absent in those activated at 950°, is to be associated with the tightly bound water layer found on the charcoals activated at the lower temperature. The amount of water found on charcoals A, B, and $C_2$ is approximately the amount required for a unimolecular layer of adsorbed molecules, and this is almost completely driven off on raising the temperature of the charcoals to 950°; the authors previously cited find that active charcoals activated or ignited at this temperature lose the capacity for adsorbing alkalis but are now capable of adsorbing inorganic acids.

Scrutiny of the previous investigator's results yields some interesting data as to the manner in which a water layer may be formed on their " acidic " charcoals. For instance, Kolthoff (*loc. cit.*) found that the best way to produce the " acidic surface " is to heat in a stream of *moist* oxygen at 400°, and that the acidic surface was unaffected by heating in a vacuum at temperatures below 500°. Even 50 hours' heating at 500° did not affect the acidic surface, but heating at 575° or 600° for 24 hours considerably reduced this type of surface, as indicated by the reduced adsorption of sodium hydroxide. This is of considerable interest since the analyses in the present investigation show that (apart from water adsorbed from the atmosphere at room temperature and removable in the cold), the first considerable rush of desorbed water occurs at about 575°. Kolthoff also found that the " acid surface " could be produced to some extent by prolonged boiling in conductivity water, and that while such charcoal and 950°-activated charcoal possessed dissimilar catalytic properties for the oxidation of potassium ferrocyanide by oxygen, the former could be made to resemble the latter in catalytic properties by heating it for 10 hours at 620°.

Recently, Miller (*J. Physical Chem.*, 1932, **36**, 2967) has found that a charcoal activated at 500° results in an " acid charcoal " which adsorbs sodium hydroxide, but one heated at 950° exhibits negative adsorption of alkali; if the latter is subsequently activated at 500°, negative adsorption of alkali still persists. He concludes that " for rapid formation of the complex acid it is necessary to heat the charcoal at 300—400° in the presence of air and *water vapour*."

The results obtained from the analyses in this investigation and the information obtained from the sources mentioned above make it possible to conclude that the " acid oxide " or " acidic substance " which confers on charcoal activated at 500° the property of adsorbing alkali hydroxides is the tightly bound unimolecular layer of adsorbed water which has been found to exist by the author.

*Origin of the Water Layer.*—The inactive charcoals obtained by carbonisation of sugars or other organic substances evolve, on being degassed, considerable quantities of non-condensable gases and water vapour. It is generally agreed that inactive charcoals differ from active charcoals in that the former have their surfaces " poisoned " by the adsorption of higher hydrocarbons and/or polymerised substances produced in the carbonisation of the original material, and that the process of activation consists in the oxidation and removal of these poisons. These hydrocarbons are oxidised to oxides of carbon and water and thus, since the water is formed right on the surface and considerable quantities of heat are evolved by the exothermic oxidation reactions, the water is in an extremely favourable condition for immediate adsorption in the form of a high-temperature adsorbed layer. Under these conditions it appears that the water competes favourably for the charcoal surface and may be selectively adsorbed.

If the water was produced by the oxidation of hydrogen which might have been occluded or adsorbed on the charcoal as one of the decomposition products in the carbonisation of the sugar, it appeared possible to adsorb hydrogen at 500° on the 950°-activated charcoal D, and then by subsequent oxidation to convert this into a high-temperature adsorbed water layer. 0·5085 G. of charcoal D was placed in the quartz tube and the air displaced by pure nitrogen, a pulsimeter being attached to the exit end to prevent the back diffusion of air. Dry hydrogen from a Kipp's apparatus was passed over the charcoal, which was maintained at 500°, for 30 minutes, and the charcoal after being cooled in hydrogen was immediately weighed; the amount of charcoal obtained was 0·2556 g. (charcoal E). Thus nearly 50% of the charcoal was lost by some interaction with the hydrogen. The charcoal E was kept for 48 hours in the atmosphere, thereby gaining 0·0280 g.; it was then analysed in the usual way, the procedure being as in Analysis 3.

*Charcoal E.—Analysis* 10.

| Streaming nitrogen. | | | Combustion in $O_2$ at 800°. | |
|---|---|---|---|---|
| Temp. of charcoal. | $H_2O$ evolved, g. | Critical temp. for condensation of $H_2O$. | Carbon, g. | $H_2O$, g. |
| Up to 250° | 0·0277 | Room temp. | 0·2346 | 0·0079 |
| ,, 500 | 0·0023 | | | |
| ,, 600 | 0·0007 | | | |
| ,, 700 | 0·0008 | | | |
| ,, 850 | 0·0012 | | | |
| ,, 970 | 0·0029 | | | |
| Total | 0·0356 | | | |

C + total $H_2O$ = 0·2781 g.
Charcoal taken = 0·2836 g.
Diff. = −0·0055 g.

It is obvious that very little water was produced by the treatment to which the charcoal was subjected. A small discrepancy (about 2%) was found between the quantity of charcoal taken for analysis and the carbon and total water obtained; this may be due to adsorption of a small quantity of the reaction complex formed by the hydrogen and charcoal (probably hydrocarbons) which was not collected in the absorption train. The amount of water evolved up to 250° corresponds very closely to the increase in weight of charcoal E on standing in the atmosphere, and is clearly due to adsorption of atmospheric water vapour at room temperature.

There is no doubt that, however the water may be formed on the 500°-activated charcoals A, B, and $C_2$, it should be possible to induce a charcoal with no adsorbed water layer to take up high-temperature adsorbed water if the appropriate method could be found. An attempt was therefore made to place water directly on the 950°-activated charcoal D at 500°. Nitrogen was bubbled through a flask containing good distilled water which was heated to 80°. The moist nitrogen was then passed over 0·4067 g. of charcoal D for 15 minutes. After standing over-night in the atmosphere, the charcoal weighed 0·4071 g. The small change in weight does not indicate that no action occurred, since it is well known that water vapour can oxidise charcoal; the close concordance in weight is thus purely accidental. The analysis was as follows :—

*Analysis* 11.

| | | | | |
|---|---|---|---|---|
| Up to 250° | 0·0117 | Room temp. | 0·3747 | 0·0075 |
| ,, 500 | 0·0012 | | | |
| ,, 600 | 0·0069 | | | |
| ,, 700 | 0·0003 | | | |
| ,, 850 | 0·0018 | | | |
| ,, 950 | 0·0027 | | | |
| Total | 0·0246 | | | |

C + total $H_2O$ = 0·4068 g.
Charcoal taken = 0·4071 g.
Diff. = −0·0003 g.

The results indicate that a small but appreciable quantity of high temperature adsorbed water is evolved at 500—600°. It has been shown by Taylor and Benton and their respective co-workers that high-temperature adsorption is a slow process, and there is little doubt that if the water had been passed over the charcoal for a much longer time, a considerably greater quantity of water would have been adsorbed.

While the published analyses of charcoals are mainly concerned with specimens containing mineral impurities and elements such as sulphur and nitrogen, yet a critical examination of a number indicates that the oxygen and hydrogen are present nearly in the proportions of water, if allowance is made for the possible combination of some of the hydrogen and nitrogen in the form of ammonia. Barker's analyses (*Ind. Eng. Chem.*, 1930, **22**, 926) of active charcoals containing impurities, besides considerable quantities of ash, are significant. His final results are based on an ultimate analysis of three ash-free and " moisture-free " charcoals, the moisture being obtained by heating in nitrogen to 150° and then in a vacuum to only 300°. It is seen from the following table that the oxygen and hydrogen are present in nearly the proportion 8 : 1, and since the oxygen was obtained by difference, it includes the total errors of experiment.

| | | | |
|---|---|---|---|
| C, % | 95·66 | 90·14 | 94·50 |
| H, % | 0·64 | 0·76 | 0·62 |
| O (by diff.), % | 3·74 | 9·10 | 4·88 |

The results obtained by Owaga (*Biochem. Z.*, 1926, **172**, 249) are even more illuminating, and their significance has been missed by all investigators; they are of special value since the charcoals were prepared from pure organic compounds and contained no elements other than carbon, oxygen, and hydrogen.

*Composition of Charcoals before and after Activation.*

| | Composition, %. | | | | | |
|---|---|---|---|---|---|---|
| | Normal. | | | After activation. | | |
| Source of charcoal. | C. | O. | H. | C. | O. | H. |
| Sucrose | 95·2—95·3 | 4·0—4·1 | 0·1 | 95·4—95·5 | 4·1 | 0·5 |
| Naphthalene | 90·9—90·7 | 7·8—7·9 | 1·3—1·4 | 91·8 | 7·4 | 0·8 |
| Paraffin | 89·7—90·0 | 8·8—9·2 | 1·1—1·2 | 90·0 | 8·9 | 1·1 |

After activation the oxygen and hydrogen are very closely in the ratio of 8 : 1, even although the sugar alone contained oxygen, the other initial materials being hydrocarbons. The results are in substantial agreement with the author's conclusions as to the nature of low- and high-temperature activated charcoals.

*Activated Adsorption of Water.*—The phenomenon of high-temperature adsorption of gases and vapours on solids has been the subject of considerable interest in recent years. This type of adsorption has been recognised to have special properties and has been called by Taylor and his co-workers " activated adsorption," since it is accompanied by high energies of activation. Many other investigators have confirmed the large heats of adsorption involved, and these large energies are accorded wide significance in the study of reaction kinetics at interfaces. There is considerable evidence for the high-temperature adsorption of water; *e.g.*, Rakovsky (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 371) found that charcoal retained water even on heating to redness in a stream of nitrogen, and Coolidge (*J. Amer. Chem. Soc.*, 1924, **46**, 625) could not recover all the water adsorbed by heating to high temperatures. Allmand and his co-workers have published numerous results on the hysteresis effects encountered in the adsorption–desorption isotherms of water vapour on charcoal, and found that even on heating to 800° all the water adsorbed at 25° could not be recovered (*J. Physical Chem.*, 1929, **33**, 1151). They also found that adsorption isotherms on three wood charcoals exhibited hysteresis, *i.e.*, imperfect recovery of sorbed water, and similar results were obtained with a sugar charcoal although this possessed no morphological structure (*ibid.*, p. 1682).

The results obtained by previous investigators can thus be explained by the high-temperature adsorbed water layer found by the author on charcoals A, B, and $C_2$. The interesting feature of the present investigation is the fact that the desorption of the water layer does not appear to be a continuous process, but is discontinuous, occurring at approximately 580°, 650°, 780°, and 940°. In Fig. 2 are shown the desorption–temperature curves for charcoals A and B. The curves are plotted on the assumption that the water evolved above 500° comes off precisely at the temperatures noted above and none at all at intermediate temperatures; the data do not, of course, lend themselves to a critical examination of this assumption, but from the observations made it is at least approximately true. The points obtained from the analyses of charcoals A and B agree remarkably well for higher temperatures and it is evident that the water layer is not all adsorbed under similar conditions, the charcoal surface appearing to be composed of a number of surfaces of different adsorptive activity with which definite quantities of adsorbed water are associated. The absolute quantities of water adsorbed at low temperatures (*i.e.*, room temperature) have no precise significance since these will depend upon the conditions of storage of the charcoal, the prevailing atmospheric water vapour pressure, and the time of exposure of the charcoal. The curves bring out very clearly the difference between low-temperature adsorbed water (from the atmosphere) and the high-temperature adsorbed water layer. There is an abrupt change in the direction of the curves (parts X and Y): the two types of adsorption are sharply differentiated and give direct evidence of the existence of an activated adsorption layer, the existence of which has been widely questioned. The stepwise character of the desorption curve of the activated adsorbed water layer is of some significance in the theory of active spots and suggests the existence of a division of the charcoal surface into parts of different potential. In this connexion it is of interest to note that Garner and his co-workers (J., 1924, **125**, 1288; 1927, 2451; 1928, 2870; *Nature*, 1924, **114**, 932) have found that the heats of sorption of oxygen by charcoal increase with the rising temperature of adsorption, indicating different states of binding of the adsorption layer. The desorption curve for the reactivated charcoal $C_2$ is shown in Fig. 3; in this case, it appears that the effect of additional reactivation is to increase the areas of the parts of the surface of higher potential as compared with those of lower potential, and so leads to an adjustment of the quantities of water adsorbed, *i.e.*, the amount of high-temperature increases at the expense of lower-temperature adsorbed water. That the adsorbed water layer appears to adjust itself to the change of surface may be accounted for by a probably high mobility of the adsorbed water molecules at the temperature of reactivation (500°).

FIG. 2.

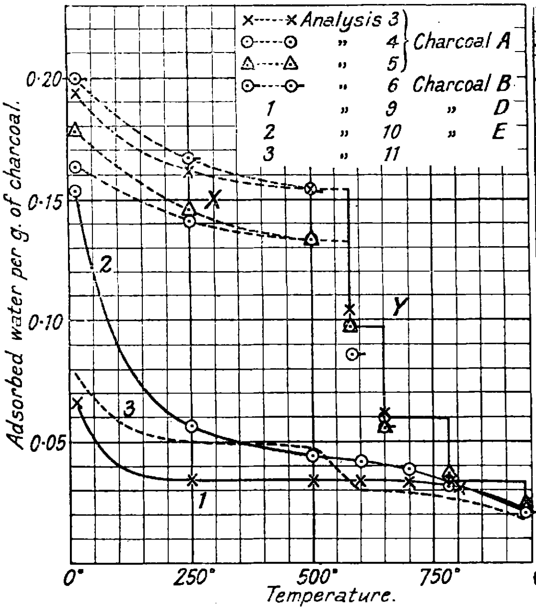
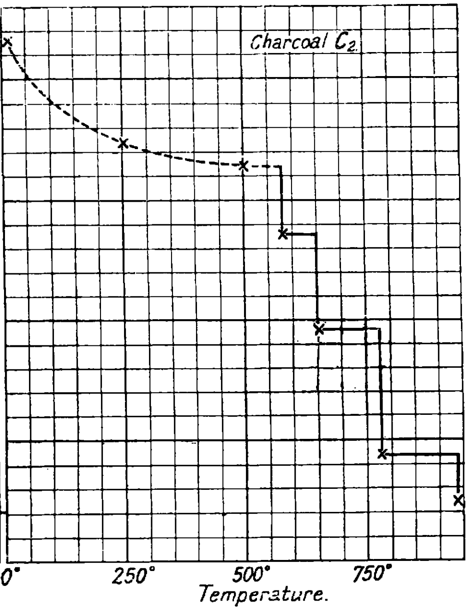


FIG. 3.



The temperature-desorption curve for 950°-activated charcoal D is shown in Fig. 2 (1).

The curve meets that of the charcoals A and B (500°-activated) at about 950° and coincides with these. The hydrogen-treated 950°-activated charcoal E gives a somewhat similar curve, Fig. 2 (2), but appears to contain considerably more low-temperature adsorbed water. The results obtained from the water vapour-treated 950° charcoal D are shown in Fig. 2 (3). A sharp bend in the curve is observed at 500—600°, due to the desorption of high-temperature adsorbed water which the charcoal was induced to take up at 500°. The interesting feature shown by all the curves is the practically constant amount of residual water retained above 950°, and this is in conformity with author's suggestion as to the identity of all the charcoals, despite different initial treatment, at temperatures above 950°. This constancy of residual adsorbed water was also observed by Allmand, Hand, and Manning (*J. Physical Chem.*, 1929, **33**, 1682) with an out-gassed specimen of charcoal; these investigators found that, although the sorption and desorption curves were distinct throughout, yet the saturation values for a series of sorption–desorption cycles were about the same, and most significantly, the final amount of bound water retained was practically constant and independent of the number of cycles gone through. They concluded " that charcoal, after saturation with water, can retain appreciable quantities of water even after outgassing to temperatures up to 800°."

The energy intercharge between adsorbed molecules and surfaces has not been extensively studied, but Garner (*Trans. Faraday Soc.*, 1932, **28**, 261) has suggested that there is a close correspondence between heats of adsorption and the potential-energy changes of the adsorbent surface. He supposes that at low temperatures only changes in rotational levels and kinetic energies would be involved, but at higher temperatures there will appear successive changes in the vibrational and electronic levels, and since these are widely separated on the energy scale they would give rise to discontinuous changes in the heats of adsorption.

Lennard-Jones (*ibid.*, p. 440) has also pointed out that there will be different activation energies for the various faces of a crystal. The results obtained in the present investigation do not enable one to calculate the heats of adsorption (or desorption) involved in the desorption discontinuities found in the high-temperature region, and further work is required to correlate these effects.

## SUMMARY.

1. Three activated ash-free charcoals have been analysed. The charcoals activated at 500° contain only carbon and water, the latter being present as an adsorption layer.

2. The water layer consists of two parts, a low-temperature adsorbed layer, desorbable at low temperatures, and a high-temperature adsorbed layer, only desorbable above 500°; the latter is the major component. The total water is equivalent to an approximately unimolecular layer.

3. The results obtained are correlated with those of other investigators, and the " oxide" theory of charcoal surfaces is shown to be fallacious. The differences in the adsorption properties of charcoals activated at different temperatures are associated with the existence or absence of the high-temperature adsorbed water layer.

4. A mechanism has been suggested for the formation of this layer during the preparation of the charcoal, and it has been shown that under proper conditions it can be formed on the surface.

5. The existence of the layer can be explained on the basis of the theory of activated adsorption, and the results are in conformity with other data which support this theory.

6. The activated adsorbed layer of water is desorbed discontinuously with temperature, and definite temperatures are associated with definite quantities of desorbed water. These discontinuities are evidence for the existence of a number of activated energies of adsorption anticipated on theoretical grounds.

This work was carried out in the Chemistry Department of the University of Edinburgh. I have again to record my thanks to Dr. J. A. V. Butler for his continued interest.

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[*Received, December* 13*th*, 1933.]