CXCIX.—*The Activation of Wood Charcoal by Progressive Oxidation in Relation to Bulk Density and Iodine Adsorption.*

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PROGRESSIVE oxidation of wood charcoal alters its sorptive capacity, but a systematic study of this alteration requires a stock material, the properties of which do not vary much from one charge to the next. To make a standard charcoal from a pure chemical compound, it may be sufficient to fix the conditions of carbonisation, but this is not true for wood charcoal, on account of the heterogeneity of wood. Accordingly, in the present work, the conditions of carbonisation were fixed only approximately, exact similarity of every quantity of charcoal taken for subsequent treatment being ensured in the following way.

The wood was carbonised in the form of cubes, which were so small that there were a very large number in a furnace charge. Since these cubes were roughly mixed and the conditions of carbonisation fixed approximately, it is likely that the charcoal from the different charges was fairly uniform. Each of these charges of charcoal was then most thoroughly mixed with all the other charges according to a definite plan, thus rendering it extremely probable that any one portion taken for subsequent treatment was a representative sample.

The standard charcoal was oxidised at various temperatures by a slow stream of air or of an oxygen–nitrogen mixture rich in nitrogen. This mode of oxidation was chosen because (a) it was a natural development from earlier rough experiments with crucibles more or less open to air; (b) it was readily controlled by varying the proportion of oxygen in the gas stream, and it allowed all the

important variables to be fixed; and (c) it seemed likely to lead to the most simple series of reactions.

The labour and time involved necessitated the examination of the treated charcoals by simple methods. Those chosen as being the most informative were the " bulk density " test and the determination of the removal of iodine from solution in benzene. These two simple tests were applied to a very large number of charcoals, all made from the standard stock.

## EXPERIMENTAL.

*Preparation of Stock Charcoal.*—Birch wood, cut into rough ½-inch cubes, was carbonised in a horizontal silica tube closed with asbestos wool. The tube was kept in a well-lagged electric furnace for 4 hours, after which it was withdrawn, allowed to cool for about ½ hour, and then unloaded. The furnace kept the interior of the tube at 400° in the absence of any charge. The charcoals obtained from 64 charges—each of which was bottled separately— were thoroughly mixed according to a plan which will be apparent from the following description for the first 8 charges. Each of the original charges 1, 2, 3, . . . 8 was divided into 8 equal parts a, b, c, . . . h. Parts 1a and 2a were mixed, giving 1.2(a). Similarly the mixed parts 1.2(b), etc., and 3.4(a), 3.4(b), up to 7.8(a), (b) . . . (h) were obtained. Then the parts 1.2(a) and 1.2(b) were themselves mixed, giving 1.2(a.b), the corresponding parts from the other charges being similarly treated. Repetition of this process gave the four mixed charges 1.2(a.b.c . . .h), 3.4(a.b.c . . . h), 5.6(a.b.c . . . h), and 7.8(a.b.c . . . h), which were now called (1.2), (3.4), (5.6), and (7.8). Each of these was divided into 16 equal parts, which were then mixed as before to give, after several mixings, the two mixed charges (1.2.3.4) and (5.6.7.8). Each was divided into 32 equal parts, which were then mixed in the same manner to give eventually the mixed charge (1.2.3.4.5.6.7.8). The mixed charge (1.2.3 . . . 64), when sieved free from dust, was the stock charcoal, the oxidation of which has been studied.

*Conditions of Heat Treatment.*—(i) *Temperature.* The temperature of the charcoal during heat treatment was taken as that given by a platinum–rhodium couple the junction of which was immediately over the pile of charcoal. Occasional regulation of a long and well-lagged wire resistance furnace prevented fluctuations of more than 5° from the required value.

(ii) *Atmosphere.* Mixtures of oxygen and nitrogen at atmospheric pressure were passed at known rates over the charcoal. The oxygen contents (by vol.) of mixtures 1, 2, 3, and 4 were,

respectively, 21, 10, 2, and 0·5%, the first being air, and the other three being supplied in cylinders by the British Oxygen Co., Ltd. —these were analysed in a Bone–Wheeler apparatus. In a short experiment, the effect of the oxygen in the 0·5% mixture appeared to be negligible. There was no reason, therefore, to use pure nitrogen.

The rate indicator was a sulphuric acid bubbler with a jet ground off square. It was protected on both sides, and the complete train was calibrated, yielding a curve showing the rate of delivery of gas in litres per hour corresponding to the number of bubbles per minute. The bubbler was quite suitable for the slow rate of 0·7 litre per hour which was nearly always used. Regulation of the rate of mixtures 2, 3, and 4 was obtained by the main needle valve. This required altering every 2—4 hours. Mixture 1 (air) was taken under a pressure of a few inches of water from the two 15-litre bottles A,A (Fig. 1). Rate regulation was effected by the cock shown, whilst the "stabilising cock" served as a steadying resistance to ensure even bubbling. The actual volume of air used was read from a scale on one of the bottles, which showed the combined contents of the bottles for various water levels.

(iii) *Time of treatment.* To define the time of treatment, the charcoal must be both heated and cooled quickly. The long horizontal containing tube (Fig. 1) was carried on platforms which formed a trolley running beyond the furnace at either end. To perform an experiment, the trolley was pushed to the left (as in the figure) and the cooling fan switched on. The weighed charge (27 g.) was loaded into the tube and pushed into a conical heap in the position shown. The tube was closed with water-cooled bungs, lubricated with glycerol, one carrying the thermo-couple, and the other the exit tube, which led to the trap and guard bubbler, and to the pump. The gas entered by a T-piece connected also to a closed manometer which was used in the preliminary displacement of air by three alternate evacuations and fillings with gas. The bubbling rate was adjusted and the cooling fan switched off. The voltage across the furnace was raised from its normal value to that of the main, *viz.*, 220 volts. The trolley was pushed to the right, so as to bring the charcoal into the middle of the furnace. The annular space between the containing tube and the furnace was closed at both ends with asbestos wool. In about 15 minutes the current was altered to that needed to maintain the desired temperature. The treatment was considered to have begun when the temperature had risen to within 10° of that required, and to have ended at the moment the trolley was run back to the left and the cooling fan switched on. Within 5 or 10 minutes, the

Diagram of Heat Treatment Apparatus

Fig. 1.

temperature indicated had fallen to 400°. At this temperature, activation is very slow. At 50° the treated charcoal was raked into a tared beaker and weighed.

(iv) *Other variables.* Variable conditions, such as size and shape of charcoal particles and disposition of apparatus, affecting the circulation of gas among the particles, were maintained roughly constant. Doubtless such irregular results as were obtained were partly due to these variations, which would be most marked when but little charcoal remained unburnt.

*Examination of the Treated Charcoals.*—After the selection of 12 representative cubes, the remainder were broken up to give a maximum yield of particles between 10 and 20 to the inch. Each block was cut into $\frac{1}{10}''$ sections, across the grain. The charcoal retained by the " 10 " sieve after this treatment was placed a little at a time in a flat mortar and tapped lightly. Most of it lay on its end grain and so split into small cubes instead of the usual thin strands or powder. The charcoal which passed the " 20 " sieve was ground in a glass mortar to yield equal quantities of " 100—200 " and " less than 200 " charcoal. The " 10—20 " size, intended for gas adsorption, has not yet been used. The "100—200" size proved convenient for " bulk-density " tests. The " less than 200 " size was used for sorption from solution.

*Determination of bulk density.* About 6 c.c. of the " 100—200 " charcoal spread over the bottom of a flat weighing-bottle remained over calcium chloride in a vacuum desiccator for about 12 hours. It was then weighed and transferred from glazed paper by a brush to a narrow test-tube of 7 c.c. capacity, graduated in tenths of a c.c. This tube was held vertically at one end of a horizontal arm which was pivoted at the other end, $21\frac{1}{4}''$ away. The arm carried a pin, bearing on a cam driven at 100 r.p.m. by a shunt motor, and so shaped that the arm and tube were gently raised and then given a clear drop of $1''$ at every revolution. After 15 minutes, *i.e.*, 1500 " taps," the tube was removed and the " bulk volume " of the charcoal read to 0·02 c.c. after carefully levelling the surface by striking the tube gently at the side with the finger. The tube, replaced in the " tapper," was given a further 500 taps, and the volume read again. Agreement worse than 0·01 or 0·02 c.c. indicated incomplete drying or sieving, and hence the need for a complete redetermination. The weight of the charcoal (in mg.) divided by the bulk volume (in c.c.) gives the bulk density.

*Determination of activity or sorptive capacity.* The iodine used was purified in the usual way and tested by titration against sodium thiosulphate solutions standardised against pure recrystallised potassium dichromate. The benzene was purified according to

Richards and Shipley (*J. Amer. Chem. Soc.*, 1914, **36**, 1825; 1919, **41**, 2002).    The solutions of iodine in benzene were estimated by direct titration with sodium thiosulphate in presence of aqueous potassium iodide.    As seen by a " daylight " lamp, the disappearance of the pink colour from the benzene layer was quite sharp even with $N/100$-solutions.    Fifty or 100 determinations were made at a time by the following method.    Soft-glass test-tubes were cleaned, dried, numbered, and weighed, and about 0·25 g. of charcoal was weighed roughly into each.    After drying in a vacuum desiccator, the tubes were quickly stoppered with compressed cotton wool, which was not removed until a rider adjustment sufficed to complete the weighing.    The weighed tubes were placed in a numbered rack and each was drawn out.    After solution had been added in the proportion of 100 c.c. per g. of charcoal, the tubes were sealed with a hand blow-pipe.    After being shaken for a definite period, each tube was tapped so as to remove charcoal and solution from the tip and then put in its place in a numbered rack.    Soon the suspended charcoal settled, the tip was cracked off, and the clear solution decanted and titrated.

*Nomenclature.*    All the treated charcoals are numbered as follows.    First, a number expressing the temperature at which the charcoal was treated, *e.g.*, 500, 600 . . . 900; secondly, separated from it by a stroke (/), a number, of four digits, expressing in litres the total volume of oxygen, at atmospheric pressure and room temperature, passed over the charcoal at the standard rate of 0·7 litre per hour, *e.g.*, /00·01 or /12·30.    Thus, a charcoal treated at 0·7 litre per hour for 10 hours at 600° with gas containing 2% of oxygen would be labelled 600/00·14.    If a rate other than 0·7 litre per hour were used, a special note is added, *e.g.*, 500/02·38 (14 l./hr.).

*Properties of the Treated Charcoals.*—(1) *Appearance.*    Every block appeared shrunken.    The following general statements may be made : (*a*) For 2 or 3 litres of oxygen or less, the charcoal was harder and, although still definitely black, had acquired a slight lustre.    This was most pronounced at high temperatures.    (*b*) For 4 or 5 litres of oxygen or more, the charcoal seemed softer.    (*c*) At 500° and 600°, the charcoal burnt away much as sticks in a bonfire with a large, loose, white ash.    When separated from this, and cut or powdered, the charcoal was sooty black.    The three heavily oxidised charcoals treated at 600°, 600/10·29, 600/14·33, and 600/20·58, were very soft and broke up to an intensely black soot.    (*d*) At 800° and 900°, the charcoal burnt away without much separation of loose ash.    The cubes compacted and decreased in size until there remained a tiny grey cube; this was very fragile, but

was sometimes removable from the tube, and must have been nearly all ash. The heavily oxidised charcoals were soft but not sooty. Those treated at 900° were noticeably flaky. (e) The 700° charcoals seemed intermediate between those mentioned in (c) and (d).

(2) *Rate of sorption of iodine from benzene solution, and the ageing effect.* In all the experiments with freshly treated charcoal the duration of shaking was 22 hours. According to Davis (J., 1907, **91**, 1663), McBain (*Trans. Faraday Soc.*, 1919, **14**, 202), and others,

FIG. 2.

*Rate of sorption of iodine from N/10-solution in benzene by four different charcoals.*
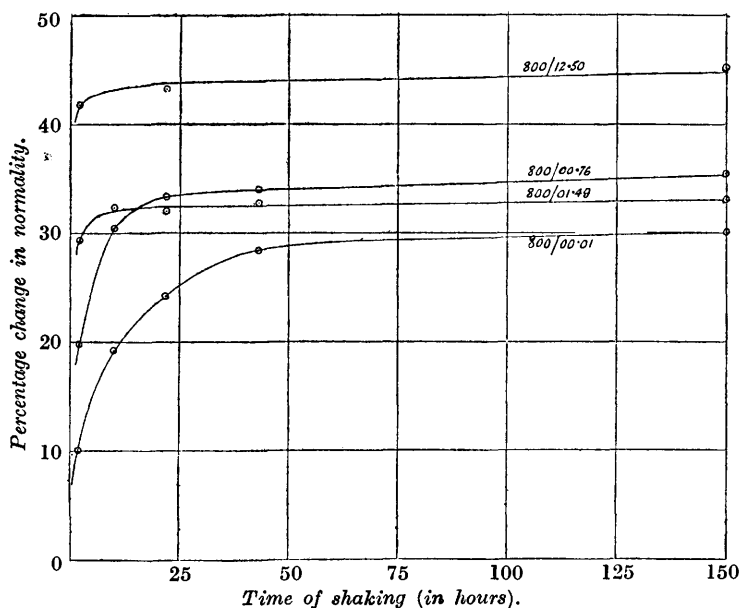


adsorption should be complete in a shorter time, and absorption not noticeable until after a much longer time. Some peculiar isotherms for charcoals prepared at 600°, 700°, and 800° with little oxygen threw doubt on this. Accordingly, it was decided to determine the rate of sorption from $N/10$-solution by the four typical charcoals 800/12·50, 800/01·49, 800/00·76, and 800/00·01. The results are plotted in Fig. 2.

The distinction between *ad-* and *ab-*sorption is not clear. Although the order of figures is the same at 22 as at 150 hours' shaking, yet the absolute values are very different. In particular, the figure for charcoal 800/00 01 at 22 hours is 6% low. Evidently the /00·01

charcoals are exceptional. The contention of Herbst that a slow rate of sorption is due to a high density is not upheld. Other factors must be more important, for the bulk densities of 800/00·01, /00·76, and /01·49 are about the same. McBain's " cleaning " of the surface is possibly one such factor. There is an undoubted ageing effect which may account in part for the slow rate of sorption. It will be seen from the general tables that the sorption from $N/5$- and $N/10$-solution, after shaking for 150 hours with charcoals which have aged, is less than that brought about by shaking for 22 hours with freshly treated charcoals. But this ageing effect cannot account entirely for the slow rate, for the sorption from $N/20$-solutions is about the same, whilst from $N/50$-solutions it is greater when brought about by shaking for 150 hours with aged charcoals than for 22 hours with fresh charcoals. This would probably be even more marked at higher dilution. The ageing effect is irregular, for although the individual isotherms for aged charcoals with long shaking are smoother than the others, yet the isotherms for a series of charcoals are related for the short period and unrelated for the long period. There is no evidence indicating the cause or nature of the effect. It may possibly correspond, in part, to the formation of a stable carbon–oxygen complex from the catalytic carbon surface and adsorbed oxygen (see Rideal and Wright, J., 1925, **127**, 1347).

(3) *Influence of the rate of passage of gas.* This can be deduced from the general tables (for eight charcoals), but is of little interest. It is noteworthy, however, that, for a given percentage yield, the charcoals prepared with a fast gas stream are less active than those with a slow stream. It is possible that at the fast rate either some of the active carbon may be removed mechanically, or, since there may be more oxygen available at any instant, more of the active carbon formed (or freed) is burnt away or perhaps covered with a " Langmuir film " of firmly attached oxygen.

(4) *Significance of the total amount of oxygen.* It was soon found that the properties of charcoals treated at any one temperature with a gas stream of 0·7 litre per hour depended almost solely on the *total* amount of oxygen passed, and if this was kept constant, they varied comparatively slightly with the joint alteration of time of treatment and oxygen concentration. This is shown in Table I,
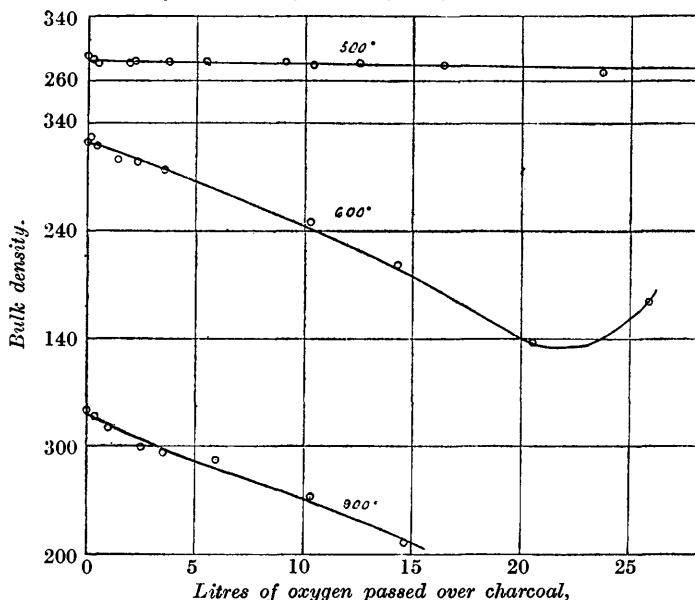
TABLE I.

Activity towards $N/10$-solutions.

| Name of charcoal. | Charcoal treated 4 hours in 2% $O_2$. | Charcoal treated 16 hours in 0·5% $O_2$. |
|---|---|---|
| 400/00·06 | 7·4 | 8·0 |
| 600/00·06 | 39·9 | 40·0 |
| 900/00·06 | 4·9 | 5·6 |

the change in activity when the total oxygen is constant being within the limits of experimental error. At the same time, during long experiments there was probably some distillation, and the effect of the change of oxygen concentration from 21% in Mixture 1 to 0·5% in Mixture 4 cannot have been entirely negligible.

(5) *Effect of temperature change and variation in the total amount of oxygen.* The yield of charcoal treated at any one temperature falls off directly with increase in the total volume of oxygen passed. There is a tendency for it to fall less quickly when but little char-

FIG. 3.

*Variation of bulk density with degree of oxidation of charcoal.*



coal remains unburnt, and less quickly at low than at high temperatures. These changes can be seen by plotting the data given in the main tables.

*The Bulk-density Curves.*—In Fig. 3 is shown the variation of bulk density with oxidation at 500°, 600°, and 900°. It will be seen that the bulk density of charcoals treated at 500° is nearly constant and independent of the amount of oxygen used. That of charcoals treated at 600° and 900° falls off regularly with oxidation. With excessive oxidation the bulk density of the charcoals treated at 600° eventually rises after passing through a minimum. This rise is probably due to a very high ash content, most of the carbon having been burnt away. Associated with it is a low

activity towards $N/10$-iodine solution. The irregular fluctuations of the bulk density of slightly oxidised charcoals are probably fortuitous. The curve for charcoals treated at $700°$ is similar to the $600°$ curve. The $800°$ curve flattens at the highest degree of oxidation used and would probably rise with further oxidation.

### Sorption of Iodine from Benzene Solution.

(i) *The " Freundlich " Constants.*—To characterise the activity of each treated charcoal, adsorption isotherms have been obtained

FIG. 4.

*Typical logarithmic adsorption isotherms for charcoals treated at $600°$.*
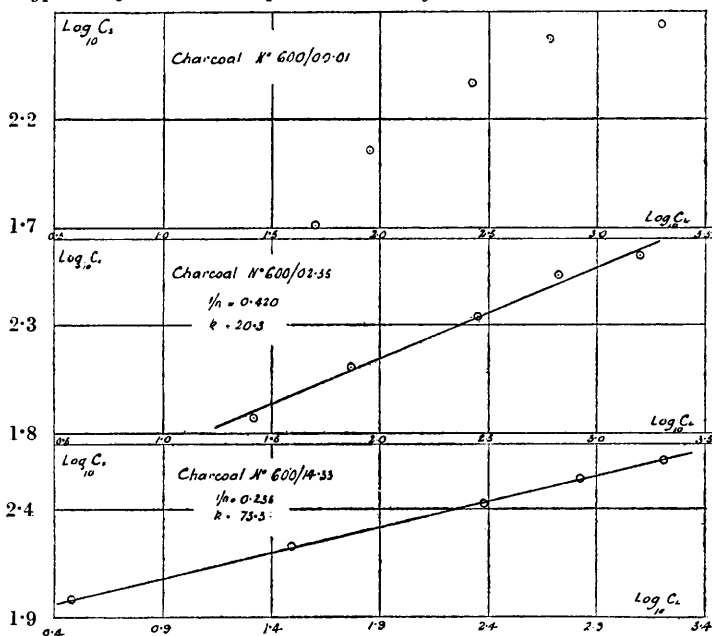


with iodine in benzene solution. The concentrations used were $N/5$, $N/10$, $N/20$, $N/50$, and $N/100$ with 22 hours' shaking, and $N/5$, $N/10$, $N/20$, and $N/50$ with 150 hours' shaking. The concentration in the solid phase, $C_S$, is expressed in terms of c.c. of $N/100$-solution containing the iodine adsorbed per g. of charcoal; and that in the liquid phase, $C_L$, is similarly expressed per 100 c.c. of solution. No account has been taken of the removal of the benzene by the charcoal. Curves were drawn showing the change of $\log_{10} C_S$ with $\log_{10} C_L$ for each charcoal. Most of these curves are fair straight lines, and from them have been calculated the constants in the Freundlich equation ($C_S = kC_L^{1/n}$), $k$ being the

concentration in the solid phase when that in the liquid is equal to unity, and $1/n$ the slope of the line. The three curves in Fig. 4 are representative of those obtained from experiments with 22 hours' shaking. With 150 hours' shaking, there was, on the whole, considerably closer approximation to the straight line. The curve for charcoal 600/00·01 is an extreme example of the curvilinear form obtained with very slightly oxidised charcoals treated at temperatures below 850°. Most of the charcoals treated at 500° give similar curves. The other two curves are fair samples of the bulk; that of charcoal 600/02·35 is the first of the 600° curves from which constants have been calculated.

The interpretation of the changes in these constants ($k$ and $1/n$) depends, in the first place, on the following considerations. For any one isotherm, $1/n$ is a characteristic constant and depends only on the ratio of the units chosen for $C_S$ and for $C_L$. Its variation, from one isotherm to another, is not even dependent on the particular value of this ratio, provided this is kept constant. On the other hand, $k$ depends on the magnitude of the units chosen. Further, since two isotherms will cross each other at concentrations higher or lower than $C_L = $ one unit, according to the magnitude of the unit, therefore the *relative* value of $k$ for the two isotherms will also change. Now $C_L$ is expressed in very small units, so that it happens that the crossing point of most of the isotherms is at liquid concentrations higher than $C_L = 1$. (This can be seen by plotting, and follows also from the reciprocal variation of the constants from one isotherm to another, which is most marked— see curves in Fig. 5.) Hence a change in the value of $k$, accompanied as it is by a reciprocal change in the value of $1/n$, actually indicates a change in sorption at low concentrations, whilst the magnitude of $1/n$ indicates the extent to which the sorption falls off at higher concentrations compared with simple proportionality.

(ii) *Variation of the Constants with Temperature and Total Amount of Oxygen.*—For 22 hours' shaking, the variation of $k$ and $1/n$ with the volume of oxygen passed over the charcoal at 600°, 700°, 800°, 850°, and 900° is shown by the curves in Fig. 5. The scales of plotting are, of course, arbitrary; therefore, the maxima and minima and the points of inflexion are the only characteristic features. The curves for 600° are traced no nearer to the zero oxygen axis than 2·35 litres of oxygen, because the shape of the isotherms of the less oxidised charcoals did not permit the evaluation of the constants. The values for the slightly oxidised charcoals at 700° and 800° are from lines on the logarithmic graphs drawn through points derived from measurements with $N/5$-, $N/10$-, and $N/20$-solutions, the experiments in which the shaking was pro-

longed to 150 hours having shown that the systems with the more dilute solutions were probably far short of equilibrium. Very few of the 500° charcoals give isotherms from which constants can be calculated even after the long period of shaking. This slowness in attaining equilibrium was one of the important points brought out by the experiments with long shaking. The other was the clear demonstration of the ageing effect. Unfortunately, as previously

FIG. 5.

*Change of Freundlich constants with degree of oxidation of charcoal.*
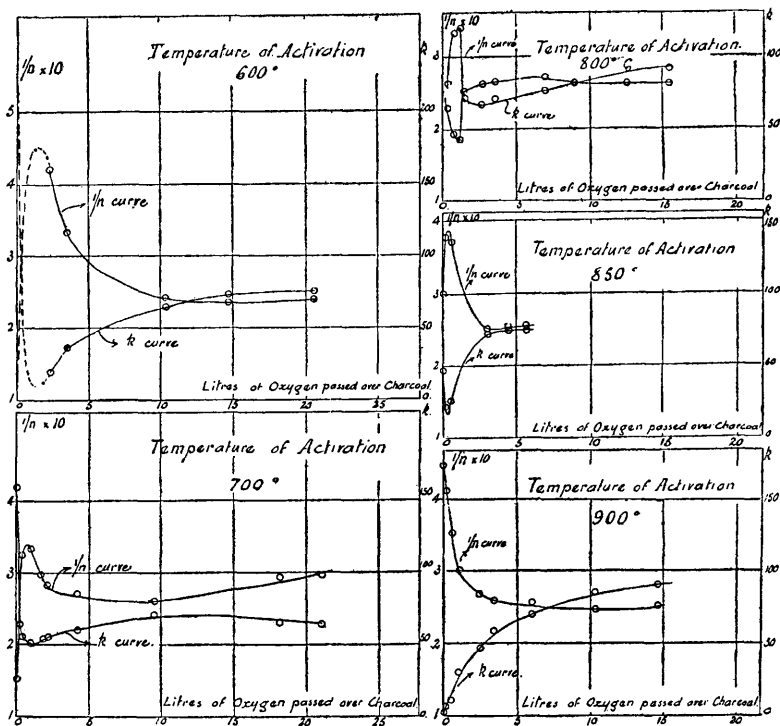


mentioned, the irregularity of this effect has concealed the relations of the constants obtained from these experiments with 150 hours' shaking.

The reciprocity of the $k$ and $1/n$ curves shows, as already stated, that, in general, the isotherms cross one another at concentrations higher than $C_L = 1$, *i.e.*, higher than $C_L = 0.0001N$. On comparing all the isotherms, many crossing points will be found between $C_L = 0.0002N$ and $0.193N$, *i.e.*, within the range which includes $N/10$-, $N/20$-, and $N/50$-solutions, one of which is frequently used

for determining activity (compare Ruff, *Z. angew. Chem.*, 1925, **38**, 1164; Berl and Wachendorff, *Koll. Z.*, Special No., April, 1925, pp. 36—40). From this it follows that determinations of activity made at only one concentration are, in general, misleading.

The curves obtained by plotting $k$ and $1/n$ as ordinates against volumes of oxygen as abscissæ are steepest near the zero oxygen axis. There is a family resemblance between the curves at the five temperatures. On the zero oxygen axis, the highest value of $k$ is probably at 600°, as indicated by the dotted line suggested for the shape of the 600° curve over the range where no figures are obtainable. From 600° the initial value of $k$ decreases continuously with temperature to a very low value at 900°. The subsequent fall of $k$ with increasing value of oxygen also varies with temperature in the same sense from 600° to 850° inclusive. At 850°, the fall is small, whilst at 900° it is non-existent; $k$, at that temperature, increases continuously with the volume of oxygen from its very low initial value to about the same as that attained by the 800° curve. This continuous increase in $k$, which forms the whole curve at 900°, corresponds to the only clearly marked feature of the curves at the other temperatures after the initial fall in the $k$ values has been passed. The curves at 700° and 800° certainly have a more complicated form, but it cannot be decided whether this is due chiefly to experimental error or not. It is rather remarkable that these derived curves, expressing the properties of so variable a substance as charcoal, should show resemblances as clearly as they do. The $1/n$ curves exhibit somewhat similar resemblances.

The extent of the variation of $1/n$ is surprising when it is recalled that the charcoals which show it have all been prepared from the same stock charcoal; for the magnitude of $1/n$ expresses, as already stated, the extent to which sorption falls away at high concentrations from simple proportionality, and must indicate a change in type or disposition of surface rather than the mere enlargement which might be expected to result from progressive oxidation.

Strictly, since $k$ and $1/n$ are characteristic of the whole system and not of the charcoal alone, it is difficult to interpret their changes in terms of changes in the charcoal. (It may be recalled that Firth, *Trans. Faraday Soc.*, 1921, **16**, 434, found that the constants for the system iodine–*benzene*–charcoal differed from those for the system iodine–*chloroform*–charcoal.) Besides this difficulty, there is the solvent correction, which is uncertain, although of little importance at the low concentrations used. If, however, the constants $k$ and $1/n$ are conceded to be relatively characteristic of the charcoal, then the following suggestions may be put forward to account for their variation.

*Theory of the Variation of the Freundlich Constants.*—The changes from one charcoal to another, which may be responsible for the observed variation of $k$ and $1/n$, will first be considered. Since the solution wets the charcoal there must be a definite attraction between the two. Further, the equilibrium concentration of iodine in the bulk of the solution is less than that at the solution–charcoal interface; hence, there is a decrease of surface energy accompanying adsorption, and more energy is liberated in the adsorption of iodine by the charcoal than in the adsorption of benzene. This will hold whatever be the mechanism of the adsorption, whether the attracting field of force above the charcoal surface is uniformly distributed over the surface or localised at active spots, whether it extends for only one molecular diameter or for many, or whether it varies so that in effect only every $x$ atoms of carbon can attract one adsorbed molecule. An increase of available surface per gram of charcoal would merely increase the value of $k$.

A change in the value of $1/n$ would entail either (i) a change in the field of force, involving the creation of, or an alteration in, an interference effect between the adsorbed molecules; or (ii) a change in the relative importance of two or more types of attraction.

It is easy to see that (i) might be brought about either by a molecular rearrangement of the surface producing a change in the closeness of packing of the adsorbed molecules or by a change in the disposition of the available surface producing locally, according to the size and shape of the capillaries, a change in the closeness of packing.

Since adsorption depends on the specific attraction of the carbon in charcoal, it follows that if there is more than one type of carbon, as Chaney assumed (*i.e.*, presumably, more than one type of crystal lattice), then a change in the proportions of these types would bring about change (ii) above.

Rideal and Wright (*loc. cit.*) distinguish three types of surface, and it may be that investigation of the charcoals on the lines of their method would have furnished a satisfactory characterisation. The attempt, however, has been made to interpret the results obtained in the present investigation on the basis of change (i) above.

A brief summary of the variations of $k$ and $1/n$ is of use in considering the corresponding variations in the charcoal: (i) $1/n$ varies from one charcoal to another; (ii) $k$ and $1/n$ vary reciprocally, as a rule; (iii) $k$ and $1/n$ always vary simultaneously; (iv) the $k$ and $1/n$ curves for 600°, 700°, 800°, and 850° charcoals can most readily be built up from simple curves of two quantities, one of which decreases, whilst the other increases with oxidation. Now

bulk density decreases with oxidation, except that with excessive oxidation it has been shown for charcoals prepared at 600° and 700° to increase again after passing through a minimum. Philip, Dunnill, and Workman (*loc. cit.*), and others, have correlated bulk density with activity, and have suggested that with decrease of bulk density there is an *increase of available surface* which accounts for the observed increase in activity. This view seems reasonable, and is further supported by the present work if we exclude for the moment those charcoals prepared with very little oxygen, *i.e.*, less than 1 or 2 litres, at temperatures below 900°. In particular, the view is supported by the decreasing sorption (from $N/10$-solution *) which accompanies increasing bulk density of the most highly oxidised charcoals prepared at 600° and 700°. If this view is accepted, then both the increase of $k$ and the decrease of $1/n$ receive a reasonable explanation. We have only to picture, along with the increase of the extent of surface, a change in the disposition which would increase the packing effect. This packing effect would obviously be more important at high than at low concentrations, so its increase would lead to a decrease of $1/n$. It is easy to see that if the oxidation increased the surface by rendering more and more capillaries available, then in these capillaries a packing effect would not be unlikely.

In seeking a quantity likely to *decrease* with oxidation, in order to suggest a change in the charcoal responsible for the changes in the first part of the $k$ and $1/n$ curves, the rapidity of these changes must be borne in mind. The quantity must alter so as to bring about a large change at 600° and 700°, a smaller change at 800° and 850°, and none at all at 900°; further, its alteration must bring about these changes over a range of oxidation, over which other quantities, such as bulk density and yield, vary very little. It is suggested that this quantity must be the effective number of attracting centres per unit of surface. It may also be described as a particular configuration of the surface giving *in effect* a large number of active centres, and may correspond to what Chaney describes as a particular modification of carbon in an " active " state. We may readily imagine that this quantity would have quite different values, initially, at different temperatures, as is required, varying from a low value or zero at 900° to a maximum at 600°. It is not difficult to see that the effect of oxidation might well be to decrease this quantity rapidly, either by the removal of the active centres (or the " active carbon ") or by the formation of a firm " Langmuir adsorption compound." Since the bulk

* There was not sufficient charcoal left after oxidation to determine the sorption from solutions of other concentrations.

density of the unoxidised charcoals is high, therefore the available surface is probably small, so that the large number of active centres involves a large number of these centres per unit area, and therefore favours a large packing effect, giving a low value of $1/n$ and a high value of $k$. The rapid decrease in the number of active centres with oxidation causes a corresponding decrease in $k$ and increase in $1/n$.

*Iodine in benzene solution : 22 hours' shaking.*
*Percentage change in normality at various concentrations.*

| Charcoal No. | Bulk density. | Yield, %. | $N/100$. | $N/50$. | $N/20$. | $N/10$. | $N/5$. |
|---|---|---|---|---|---|---|---|
| 500/00·01 | 302 | 76·6 | 44·2 | — | — | 23·8 | 14·7 |
| 500/00·25 | 299 | 76·4 | — | — | — | 26·6 | 15·5 |
| 500/00·46 | 296 | 76·4 | 41·5 | — | — | 27·0 | 15·8 |
| 500/01·13 | 309 | 74·9 | — | — | — | 27·4 | — |
| 500/01·83 | 295 | 73·8 | — | — | — | 26·2 | 15·8 |
| 500/02·14 | 298 | 74·5 | 33·9 | — | — | 26·9 | 15·4 |
| 500/03·76 | 296 | 69·4 | 43·3 | — | — | 29·9 | 16·0 |
| 500/05·46 | 297 | 66·0 | 44·8 | — | — | 32·0 | 17·1 |
| 500/09·01 | 296 | 60·8 | 49·8 | — | — | 31·8 | 17·3 |
| 500/10·33 | 292 | 56·7 | — | — | — | 20·5 | 16·5 |
| 500/12·50 | 294 | 53·0 | 55·6 | — | — | 30·6 | — |
| 500/16·34 | 293 | 47·0 | — | — | — | 27·6 | 16·7 |
| 500/23·63 | 285 | 31·2 | 66·1 | — | — | 28·4 | 18·2 |
| 500/31·16 | 294 | 16·7 | 77·2 | — | — | 29·3 | 17·4 |
| 600/00·01 | 322 | 74·1 | 51·1 | 56·5 | 46·4 | 38·9 | 21·6 |
| 600/00·06 | 325 | 82·6 | 55·4 | — | — | 39·9 | — |
| *600/00·06 | 322 | 73·9 | — | — | — | 40·0 | 21·8 |
| 600/00·22 | 326 | 71·9 | — | 63·2 | — | 41·2 | 23·4 |
| 600/00·28 | 321 | 73·9 | 58·9 | 61·2 | 48·8 | 41·0 | — |
| 600/00·42 | 316 | 73·9 | — | — | — | 41·2 | — |
| 600/00·59 | 310 | 71·9 | 67·5 | 72·5 | — | 41·3 | — |
| 600/01·40 | 306 | 68·9 | 73·6 | 74·1 | 55·4 | 40·2 | 22·5 |
| 600/02·35 | 302 | 68·5 | 74·0 | 63·2 | 43·3 | 34·2 | 20·5 |
| 600/03·53 | 296 | 66·0 | 85·4 | 69·8 | 47·0 | 32·5 | 20·0 |
| 600/10·29 | 248 | 61·4 | 94·8 | 79·5 | 48·0 | 32·5 | 18·7 |
| 600/14·33 | 208 | 40·4 | 96·95 | 84·4 | 52·2 | 33·9 | 20·4 |
| 600/20·58 | 138 | 24·8 | 96·6 | 84·0 | 54·3 | 36·6 | 21·2 |
| 600/25·87 | 174 | 15·9 | — | — | 53·7 | 33·0 | — |
| †600/05·88 | 309 | 66·0 | — | — | — | 25·0 | — |
| ‡600/11·76 | 298 | 50·4 | — | — | — | 27·2 | — |
| 700/00·01 | — | 72·3 | — | 86·2 | 67·7 | 41·0 | 23·8 |
| 700/00·20 | 320 | 70·7 | 96·8 | 82·5 | 63·6 | 40·4 | 27·6 |
| 700/00·39 | 337 | 71·9 | — | 77·0 | 58·7 | 43·9 | 27·6 |
| 700/00·92 | 324 | 70·5 | 94·8 | 78·3 | 61·0 | 41·8 | 25·8 |
| 700/01·74 | 316 | 68·9 | 96·5 | 74·3 | 54·7 | 34·7 | 23·4 |
| 700/02·14 | 308 | 67·0 | — | 77·4 | 52·7 | 33·5 | 21·7 |
| 700/04·22 | 289 | 61·5 | 98·1 | 79·0 | 50·4 | 34·2 | 21·6 |
| 700/09·49 | 256 | 47·4 | 98·4 | 84·6 | 55·2 | 35·9 | 23·2 |
| 700/12·39 | 236 | 37·4 | — | — | — | 39·6 | 23·5 |
| 700/18·14 | 206 | 26·3 | 98·5 | 86·0 | 56·8 | 41·2 | 26·2 |
| 700/21·06 | 199 | 17·8 | 97·3 | 86·5 | 58·2 | 42·0 | 26·1 |
| 700/25·33 | 237 | 4·1 | — | — | — | 34·2 | — |

*     16 Hours.          †  7 Litres per hour.          ‡  14 Litres per hour.

| Charcoal No. | Bulk density. | Yield, %. | $N/100$. | $N/50$. | $N/20$. | $N/10$. | $N/5$. |
|---|---|---|---|---|---|---|---|
| 800/00·01 | 333 | 68·9 | 59·0 | 58·7 | 43·9 | 31·7 | 18·2 |
| 800/00·11 | 315 | 67·8 | — | — | — | 33·6 | — |
| 800/00·21 | 313 | 66·7 | 95·4 | — | — | 33·7 | 21·1 |
| 800/00·35 | 310 | 63·4 | 95·6 | 82·2 | 52·4 | 35·4 | 21·4 |
| 800/00·76 | 331 | 67·0 | 84·9 | 76·5 | 54·2 | 41·0 | 23·2 |
| 800/01·13 | 325 | 65·2 | — | 74·8 | 52·0 | 38·4 | 22·8 |
| 800/01·49 | 318 | 63·0 | 96·6 | 84·2 | 52·7 | 34·0 | 20·5 |
| 800/02·77 | 293 | 58·2 | 97·6 | 87·6 | 56·6 | 33·8 | 22·3 |
| 800/03·57 | 286 | 53·8 | 97·7 | 88·4 | 59·2 | 39·0 | 24·7 |
| 800/06·91 | 256 | 39·6 | — | 90·2 | 63·2 | 42·2 | 26·6 |
| 800/08·84 | 240 | 32·2 | 97·6 | 90·0 | 61·4 | 43·0 | 25·9 |
| 800/12·50 | 216 | 17·4 | 97·6 | 90·8 | 66·4 | 45·8 | — |
| 800/15·48 | 210 | 10·7 | 97·8 | 90·7 | 66·5 | 46·1 | 30·0 |
| 850/00·01 | 330 | 72·2 | — | — | 47·3 | 26·6* | 20·4 |
| 850/00·09 | 321 | 65·6 | 78·2 | — | 38·2 | 30·5 | 18·4 |
| 850/00·59 | 310 | 62·2 | — | 61·3 | 41·2 | 29·2 | 19·1 |
| 850/03·05 | 291 | 54·5 | 97·2 | — | 56·0 | 36·4 | 23·1 |
| 850/04·45 | 275 | 45·6 | 97·3 | — | 57·0 | 38·1 | 23·9 |
| 850/05·67 | 266 | 41·9 | 97·1 | — | 58·9 | 38·9 | — |
| 900/00·01 | 330 | 70·5 | 16·1 | 11·5 | — | 4·8 | 3·3 |
| 900/00·06 | 327 | 71·5 | — | — | — | 4·9 | — |
| †900/00·06 | 328 | 71·1 | — | — | 9·9 | 5·6 | — |
| 900/00·22 | 326 | 68·2 | 26·3 | 22·6 | 17·7 | 9·6 | 7·0 |
| 900/00·28 | 334 | 70·0 | — | — | — | 10·0 | — |
| 900/00·59 | 319 | 68·5 | 45·1 | 36·7 | 18·9 | 12·2 | — |
| 900/01·03 | 316 | 66·0 | 72·3 | 58·4 | 35·1 | 22·7 | 12·9 |
| 900/02·35 | 296 | 60·0 | 88·0 | 71·1 | 41·6 | 28·2 | 16·3 |
| 900/03·52 | 292 | 53·8 | 93·0 | 79·0 | 49·0 | 32·5 | 19·8 |
| 900/05·88 | 279 | 41·2 | 93·9 | — | 56·7 | 37·8 | 26·5 |
| 900/10·29 | 254 | 29·6 | 97·9 | 90·8 | 62·7 | 41·2 | 25·2 |
| 900/14·70 | 210 | 14·1 | 98·0 | 93·6 | 68·6 | 43·2 | 29·1 |
| ‡900/05·88 | 296 | 48·9 | — | — | — | 27·5 | — |
| §900/11·76 | 276 | 31·1 | — | — | — | 34·8 | — |

* In $N/8$-solution.  † 16 Hours.  ‡ 7 Litres per hour.  § 14 Litres per hour.

It must be admitted that the evidence for these changes from one charcoal to another with oxidation is not decisive. Further work is needed which should be sufficiently accurate to permit an examination of the $k$ and $1/n$ curves in detail—an examination not warranted by the accuracy of the present work, which has, however, fixed the general shape of the curves with considerable certainty.

*Summary.*

A large quantity of wood charcoal has been prepared and mixed so as to give a substantially uniform product.

Some 80 samples have been oxidised by oxygen–nitrogen mixtures under regulated conditions. The following properties of the oxidised charcoals have been determined : Appearance, bulk density, percentage yield, sorptive capacity for iodine in benzene solution, and rate of sorption.

Sorption isotherms have been determined for 22 and for 150

*Iodine in benzene solution :* 150 *hours' shaking.*
*Percentage change in normality at various concentrations.*

| Charcoal No. | N/50. | N/20. | N/10. | N/5. | Charcoal No. | N/50. | N/20. | N/10. | N/5. |
|---|---|---|---|---|---|---|---|---|---|
| 500/00·01 | 49·4 | 36·6 | 26·7 | 16·4 | 700/12·39 | 85·6 | 57·2 | 38·2 | 23·8 |
| 500/00·25 | 47·1 | 34·8 | 26·1 | 16·7 | 700/18·14 | 85·7 | 58·0 | 40·2 | 25·5 |
| 500/01·13 | 43·7 | 33·9 | 25·9 | 16·5 | 800/00·01 | 61·6 | 47·8 | 29·4 | 19·5 |
| 500/02·14 | 44·2 | 36·6 | 27·6 | 17·8 | 800/00·35 | 83·3 | 52·7 | 33·2 | 20·3 |
| 500/07·01 | 48·6 | 40·3 | 29·2 | 18·6 | 800/00·76 | 79·4 | 55·4 | 36·4 | 21·3 |
| 500/12·50 | — | 38·9 | 29·5 | 17·7 | 800/01·13 | 75·5 | 51·4 | 34·3 | 20·3 |
| 500/23·63 | 58·1 | 39·7 | 27·7 | 18·5 | 800/01·49 | 70·9 | 51·6 | 33·1 | 19·2 |
| 600/00·01 | 74·2 | 60·2 | 35·1 | 19·7 | 800/02·77 | 85·5 | 56·7 | 37·7 | 23·9 |
| 600/00·06 | 77·5 | 56·4 | 36·8 | 20·5 | 800/03·57 | 84·9 | 57·8 | 38·7 | 24·9 |
| 600/00·59 | 80·0 | 57·2 | 37·0 | 20·7 | 800/06·91 | — | 63·9 | 43·5 | 29·0 |
| 600/01·40 | 70·9 | 55·4 | 35·6 | 20·5 | 800/15·48 | 88·1 | 68·3 | 46·7 | 31·7 |
| 600/02·35 | 69·0 | 41·5 | 31·5 | 18·3 | 850/00·01 | 72·3 | 59·3 | 39·6 | 22·5 |
| 600/03·53 | 75·5 | 46·8 | 30·7 | 18·4 | 850/00·09 | 61·8 | 39·4 | 26·3 | 17·5 |
| 600/10·29 | 76·4 | — | 29·7 | 17·1 | 850/00·59 | 69·6 | 40·9 | 30·7 | 17·5 |
| 600/14·33 | 80·8 | 51·5 | 32·6 | 20·8 | 850/03·05 | 85·4 | 58·7 | 39·7 | 26·0 |
| 600/20·58 | 80·3 | 51·7 | 34·0 | 21·4 | 850/04·45 | 84·8 | 57·8 | 39·1 | 25·5 |
| 700/00·01 | 91·4 | 59·6 | 38·2 | 21·3 | 900/00·01 | 14·8 | 8·6 | 5·8 | 3·8 |
| 700/00·39 | 82·7 | 62·5 | 39·5 | 22·9 | 900/00·59 | 33·0 | 19·8 | 13·2 | 8·9 |
| 700/00·92 | 79·8 | 59·1 | 36·9 | 21·8 | 900/01·03 | 55·2 | 33·2 | 22·1 | 14·0 |
| 700/01·74 | 81·0 | 53·9 | 33·6 | 20·0 | 900/03·52 | 72·5 | 45·0 | 30·4 | 20·3 |
| 700/02·14 | 81·9 | 51·3 | 32·7 | 19·6 | 900/05·88 | 79·1 | 52·3 | 36·1 | 22·1 |
| 700/04·22 | 81·5 | 52·1 | 33·5 | 20·7 | 900/10·29 | 89·7 | 61·4 | 42·0 | 27·6 |
| 700/09·49 | 84·6 | 55·9 | 36·4 | 23·2 | | | | | |

*Adsorption of iodine from benzene solution.*

Freundlich constants.

| Charcoal No. | 22 hours' shaking. | | 150 hours' shaking. | | Charcoal No. | 22 hours' shaking. | | 150 hours' shaking. | |
|---|---|---|---|---|---|---|---|---|---|
| | 1/n. | k. | 1/n. | k. | | 1/n. | k. | 1/n. | k. |
| 600/00·01 | — | — | 0·126 | 156 | 800/01·13 | 0·333 | 42·3 | 0·239 | 71·0 |
| 600/00·06 | — | — | 0·187 | 108 | 800/01·49 | 0·237 | 73·3 | 0·218 | 79·4 |
| 600/00·59 | — | — | 0·182 | 112 | 800/02·77 | 0·231 | 80·9 | 0·255 | 73·5 |
| 600/01·40 | — | — | 0·197 | 97·7 | 800/03·57 | 0·240 | 81·3 | 0·274 | 66·1 |
| 600/02·35 | 0·420 | 20·3 | 0·328 | 34·3 | 800/06·91 | 0·249 | 85·7 | 0·288 | 72·9 |
| 600/03·53 | 0·332 | 36·3 | 0·259 | 55·0 | 800/08·84 | 0·260 | 80·2 | — | — |
| 600/10·29 | 0·240 | 64·3 | 0·250 | 53·9 | 800/12·50 | 0·281 | 79·1 | — | — |
| 600/14·33 | 0·235 | 73·3 | 0·251 | 64·1 | 800/15·48 | 0·279 | 79·4 | 0·314 | 66·5 |
| 600/20·58 | 0·238 | 74·3 | 0·263 | 61·4 | 850/00·01 | 0·298 | 44·1 | 0·208 | 100 |
| 700/00·01 | 0·150 | 158 | 0·172 | 124 | 850/00·09 | 0·384 | 22·6 | 0·340 | 28·1 |
| 700/00·20 | 0·296 | 63·5 | — | — | 850/00·59 | 0·372 | 25·2 | 0·309 | 37·3 |
| 700/00·39 | 0·324 | 53·3 | 0·191 | 115 | 850/03·05 | 0·250 | 74·1 | 0·283 | 65·6 |
| 700/00·92 | 0·332 | 50·0 | 0·189 | 108 | 850/04·45 | 0·252 | 74·5 | 0·283 | 63·8 |
| 700/01·74 | 0·296 | 53·1 | 0·215 | 82·0 | 850/05·67 | 0·254 | 75·5 | — | — |
| 700/02·14 | 0·282 | 54·3 | 0·221 | 75·7 | 900/00·01 | 0·444 | 2·28 | 0·396 | 3·85 |
| 700/04·22 | 0·270 | 58·9 | 0·242 | 69·3 | 900/00·22 | 0·411 | 6·31 | — | — |
| 700/09·49 | 0·256 | 69·8 | 0·257 | 69·6 | 900/00·59 | 0·355 | 11·0 | 0·377 | 10·3 |
| 700/12·39 | — | — | 0·257 | 72·9 | 900/01·03 | 0·300 | 29·2 | 0·350 | 21·0 |
| 700/18·14 | 0·293 | 63·4 | 0·283 | 65·8 | 900/02·35 | 0·265 | 46·6 | — | — |
| 700/21·06 | 0·295 | 62·7 | — | — | 900/03·52 | 0·260 | 57·7 | 0·310 | 40·1 |
| 800/00·01 | — | — | 0·268 | 52·0 | 900/05·88 | 0·255 | 70·0 | 0·292 | 53·0 |
| 800/00·35 | 0·261 | 63·8 | 0·227 | 75·9 | 900/10·29 | 0·246 | 85·3 | 0·267 | 77·3 |
| 800/00·76 | 0·328 | 46·0 | 0·220 | 86·1 | 900/14·70 | 0·253 | 90·6 | — | — |

hours' shaking for each oxidised charcoal over a range of concentration from $N/100$- to $N/5$-iodine in benzene.

An ageing effect has been observed.

The isotherms are mostly parabolic.   Their Freundlich constants have been plotted against degree of oxidation of the charcoal for five different temperatures.   A study of these curves has led to suggestions explaining the changes in the charcoal with progressive oxidation.   These suggestions are based on the views of Philip, Dunnill, and Workman, and of Chaney.