

201. *Studies in Chemisorption on Charcoal. Part VI.*
The p_H of Charcoal Suspensions.

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It is well known that the adsorption and reaction of many substances on charcoal vary widely with the p_H of the solution, so much so that Hauge and Willaman (*Ind. Eng. Chem.*, 1927, **19**, 943) state that comparisons between different types of carbons are useless unless the p_H of the solution is specified. Blowski and Bon (*ibid.*, 1926, **18**, 32) measured the p_H of suspensions of commercial charcoals in water and found that they varied greatly, most charcoals being acidic, but a few alkaline; since they ascribed this to impurities in the charcoals, they recommended that p_H determinations should be used as a criterion of the purity of a charcoal. Again, Bohn (*Biochem. Z.*, 1926, **178**, 119) and Spengler and Landt

* Although the free rotation destroys the plane α and also other symmetry elements, there remain three two-fold axes perpendicular to the C-C axis, and the molecule therefore retains the symmetry D_3 . The selection rules for this symmetry are those given in the text.

† Furthermore, the frequency 1370 satisfactorily resembles similar frequencies in the methyl halides (Bennett and Meyer, *Physical Rev.*, 1928, **32**, 888). Also the calculations of Sutherland and Dennison (*loc. cit.*) are in agreement with this assignment.

‡ The analogous frequencies in acetylene and in ethylene ($\nu_{\alpha\beta}^M$ and $\nu_{\alpha\gamma}^M$) are also of such small intensity that they have not been observed.

(*Z. Ver. deut. Zucker-ind.*, 1928, **78**, 81) found that the isoelectric point of charcoals varied between p_H 5 and 9.

In previous parts of the present series (J., 1934, 1975; *Trans. Faraday Soc.*, 1934, **30**, 1094) the difference in properties between charcoals activated in oxygen at high and at low temperatures was pointed out; it is especially marked in the case of the adsorption of acids and bases, the latter being readily adsorbed by low-temperature but totally excluded by high-temperature specimens. As it was thought probable that the electrical properties of the charcoal surface must vary to some extent with those properties studied hitherto, a systematic study of the variation in p_H of charcoal suspensions with temperature of activation has been carried out.

EXPERIMENTAL.

In previous work, special, ash-free charcoals were employed, the purification of which necessitated treatments with hydrofluoric and hydrochloric acids (King and Lawson, *Kolloid-Z.*, 1934, **69**, 21). As the last traces of these acids are extremely difficult to remove, it was thought safer in the present work to use a less intensively purified material. A charcoal was therefore made by careful combustion of recrystallised sugar, and outgassed at 950° for some hours previous to activation; its ash content was about 0.2% and consisted largely of silica and ferric oxide. A suspension of the ash from 12 g. of charcoal in 10 c.c. of water had p_H 6.7. Any values for the p_H of suspensions of this charcoal which deviated considerably from neutrality were therefore not to be ascribed to its ash content.

The charcoal was activated by heating, on silica trays in a silica tube furnace heated to a definite temperature, in a stream of moist oxygen, passing at the rate of 5 c.c./min. Activation lasted, as a rule, for 18 hours, and the charcoal was then removed from the furnace, quickly cooled, weighed, and shaken with boiled-out distilled water of p_H 6.95. Experiments showed that, if it was reasonably short, the rate of cooling had no effect on the p_H of the suspension. The measurement of the p_H was then made by means of a glass electrode and valve potentiometer, all the precautions usual in this type of work being taken.

Results.—(1) *Effect of different charcoal concentrations.* The p_H of suspensions of different amounts of a single sample of activated charcoal were measured, with the following results :

Charcoal, g. per 100 c.c.	1.04	1.51	2.78	4.01	5.97	10.00	13.88
p_H	5.04	5.02	4.88	4.75	4.61	4.44	4.30

In all later determinations, suspensions containing 1 g. of charcoal per 25 c.c. were employed.

(2) *Effect of temperature of activation of the charcoal.* The p_H of suspensions of a series of charcoals, all from the same stock sample and activated at different temperatures, was measured :

Temp. of activn.	200°	200°	200°	300°	400°	515°	515°	515°	575°	600°	620°
Time of activn. (hrs.)	2	10	24	10	15	5	10	24	15	12	15
p_H	4.0	4.0	4.0	4.5	5.4	6.2	6.1	6.2	6.4	6.65	6.8
Temp. of activn.	680°	680°	680°	730°	790°	860°	920°	960°	990°	1035°	
Time of activn. (hrs.)	4	8	24	18	18	18	18	18	18	16	
p_H	6.6	7.1	7.3	7.5	8.1	8.9	9.1	8.7	8.1	7.2	

It is seen that at low temperatures the time of activation has little influence on the p_H , whereas at higher temperatures, *e.g.*, for the 680° charcoal, considerable time elapses before equilibrium conditions are established. The equilibrium values are plotted in Fig. 1.

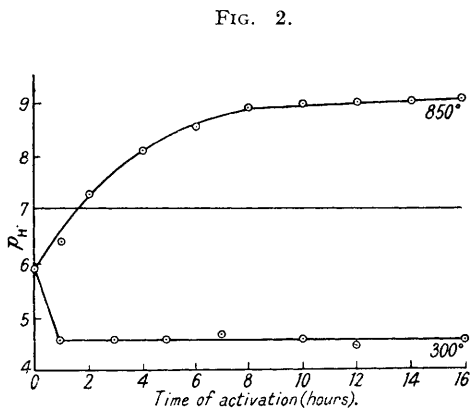
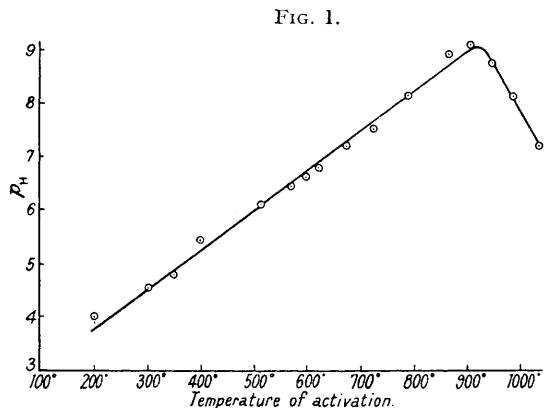
(3) *Effect of time of activation.* In view of the above results a more comprehensive study of the time required for equilibrium, with both a low-temperature and a high-temperature activated charcoal, was carried out. Results for activations at 300° and at 850° are plotted in Fig. 2.

(4) *Effect of reactivation.* In order to determine whether the values for the p_H recorded above are typical of the temperature of activation, and whether the processes leading to surface conditions which give rise to such values are truly reversible, a series of charcoals previously activated at 300°, 575°, 730°, and 920°, and whose p_H had already been measured (see preceding table), were all reactivated at 400° for 16 hours in a slow stream of oxygen, and the p_H of their aqueous suspensions redetermined. This approximated in all cases to 5.3, *i.e.*, that of a charcoal freshly activated at 400°.

(5) *Measurement of p_H of graphite suspensions.* Similar measurements were made on samples of graphite prepared from Acheson's colloidal graphite, 'aquadag,' which was coagulated with acid, filtered off, and washed with distilled water for several days. The p_H of the unactivated

product was 6.5; on activation in a stream of oxygen at 350° for 18 hours it fell to 5.3, and after heating at 750° for the same time it rose to 7.2.

(6) *Relation between adsorption of acid and alkali and p_H of commercial charcoals.* To extend the observations already made for sugar charcoal and graphite, similar measurements were made on two samples of carbon pigment black, No. 1 being a normal animal black and No. 2 a vegetable black. At the same time, the adsorption of propionic acid and of sodium hydroxide was measured on samples of these charcoals to demonstrate that the temperature of activation



of a charcoal has a fundamental effect on its power of adsorption of acids and alkalis even in the presence of impurities. The results are shown below, adsorptions being expressed as c.c. of *N*/10-solution adsorbed per g. of charcoal (actually *N*/20-solution was used) :

Temp. of activn. in O ₂ .	Time of activn., hrs.	Pigment No. 1. Adsorption of		p _H .	Pigment No. 2. Adsorption of	
		C ₃ H ₇ ·CO ₂ H.	NaOH.		C ₃ H ₇ ·CO ₂ H.	NaOH.
unactivated	—	4.9	—	3.7	1.7	0.04
300°	18	2.9	8.4	2.7	2.0	2.5
620	4	5.2	8.7	4.0	—	—
780	12	6.4	—	5.4	5.8	0.22
730 *	18	7.6	16.2	6.2	—	—

* Faster rate of oxygen flow.

(7) *Activation by carbon dioxide.* At high temperatures, carbon dioxide seems to have much the same activating action as oxygen, and it has been shown (King, J., 1934, 1977) that the effects of the two gases on the porosity of charcoal at high temperatures are of about the same order. The p_H of a series of charcoals activated at various temperatures in carbon dioxide was measured to determine whether the resultant surface was of the same kind as that produced by oxygen. The results were as follows :—

Temp.	730°	800°	860°	1000°
p _H after CO ₂ activation	6.9	7.9	8.9	8.0
p _H after O ₂ activation	7.5	8.1	8.9	8.1

(8) *Ageing of charcoals.* The stability of the surface conditions of carbon which give rise to the different electrical and adsorption effects was measured in the case of a 300° and a 750° charcoal by determining the p_H of a suspension made immediately after the completion of activation and again after different intervals of time during which the charcoals had been exposed to air at room temperature.

Temp. of activation	300°					750°				
Time of ageing, days	0	1	5	22	34	0	3	13	27	39
p _H	4.4	4.4	4.4	4.3	4.4	7.9	7.5	7.2	7.0	6.7

DISCUSSION.

It has been shown that, for sugar charcoal of low ash content, the p_H of aqueous suspensions varies widely and almost linearly with the temperature of exposure to oxygen, between room temperature and 900°. Above that temperature there is a rapid fall in the

p_H . The reversibility of the phenomenon is shown by the fact that a charcoal which has been activated at a given temperature, and thus possesses a specific p_H , could then be reactivated at another temperature and acquire a new p_H characteristic of the second temperature. This makes it impossible to ascribe the results to the presence of impurities which decompose at definite temperatures.

Similar results were obtained with graphite, but here the effect was much smaller owing, presumably, to the smaller surface area. That variation in the surface area does have some effect is shown also by the results on the p_H of suspensions containing different concentrations of charcoal. Corresponding small p_H differences should therefore be evident in charcoals activated at the same temperature but having different activities. This is indeed noticeable to a small extent in the 850° curve in Fig. 2, which shows a slow rise in p_H with time of activation after the primary, rapid rise has stopped. In the 300° curve this cannot be seen, the amount of activation at that temperature being small. The p_H of a charcoal activated at a given temperature is thus a function not only of that temperature but also, to a smaller extent, of the surface area.

With commercial charcoals the effect is again noticeable, but in the samples investigated, although it was in the same direction and of the same order, it was displaced towards the acid end of the p_H scale, probably owing to acidic impurities in the charcoal. With these samples, too, it was shown that the adsorptive power of the charcoal for acids and alkalis is parallel with its p_H , charcoals with a high p_H showing little tendency to adsorb alkalis but an enhanced power to adsorb acids, and those with a low p_H adsorbing both. Similar dependence of acid-alkali adsorption on temperature of activation has been noticed by other workers, notably by Schilow *et al.* (*Z. physikal. Chem.*, 1930, **149**, 211), who measured the decrease in caustic soda adsorption with rising temperature of activation, and by Dubinin (*ibid.*, 1930, **150**, 145), who records that, although charcoals activated in the 600—1000° region adsorbed no alkali, yet two specimens heated in oxygen to 1000° had recovered their alkali-adsorbing power to some extent. This is in line with our observation that the p_H of charcoal suspensions reaches a maximum for the 900° activation, and then decreases rapidly at higher temperatures. According to our measurements with charcoals activated at higher temperatures, a considerable time of exposure to oxygen must elapse before a surface equilibrium is established, a fact which may influence the results of some workers who used very short activation periods.

Most investigators of the adsorption of acids and alkalis on charcoal explain the results obtained after activation at different temperatures, by postulating the existence of two surface oxides, one stable on the carbon surface at high, and the other at low, temperatures. As this serves to explain and to predict some of the specific properties of charcoals, we had already adopted it as a working hypothesis, and classify the p_H results accordingly as being due to acidic or basic surface oxides. The present work gives some measure of the rate of formation of these surface oxides, the low-temperature oxide being formed almost instantaneously whereas the basic oxide (Fig. 2) is not formed in equilibrium amounts at 780° until after 8 hours' heating in oxygen. The experiments on the effect of standing in air on the p_H of charcoal suspensions (p. 891) indicate that, although the low-temperature charcoal has a constant p_H , that of the high-temperature sample falls with time, *i.e.*, the basic oxide gradually reverts to the more stable acidic form present on most pure charcoals that have stood in air for long periods. In this connexion, however, it is noteworthy that a sample of charcoal, activated for 48 hours at 950° and stored for 9 months without access to the air, retained its original surface condition, giving an aqueous suspension of p_H 8.7. In Part IV of this series (King and Lawson, *Trans. Faraday Soc.*, 1934, **30**, 1099) it was shown that, when a sample of charcoal is activated at 930° and stored in air for some time, there was a progressive increase, not only in the rate, but also in the magnitude, of adsorption of water vapour. This was ascribed to the instability of the high-temperature oxide, which gradually reverted to the stable acidic variety that had been shown to be more hygroscopic. The rate of change of adsorptive capacity for water, on standing, is of about the same order as the change in p_H .

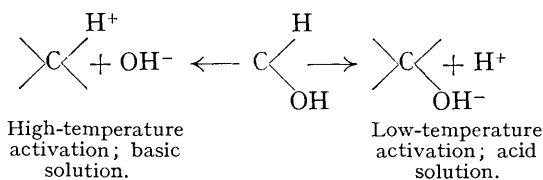
Activation in carbon dioxide has, at 800—1000°, the same effect as oxygen, the surface having thus the same constitution in both cases.

The mechanism of the production, from charcoal in contact with water, of a hydrogen- or hydroxyl-ion concentration deviating appreciably from neutrality is somewhat obscure. Either acid and alkaline materials must be formed in the charcoal and dissolved out by water, or else preferential adsorption of hydrogen or hydroxyl ions must take place, with the consequent displacement of the water balance. If the first explanation were true, it ought to be possible to filter off the charcoal from the solution without changing the p_{H} . It was found that a suspension of p_{H} 7.9 gave, on filtration, a solution of p_{H} 7.2, whereas an acidic charcoal of p_{H} 4.4 gave a solution of p_{H} 5.4. These differences on filtration may, however, well be due to the adsorption of small amounts of the acid or alkaline constituent on the filter, and so the results are inconclusive. It has been shown (J., 1933, 842) that minute amounts of an organic acid, probably oxalic acid, are produced on exposure of charcoal to air; this may contribute to the p_{H} of the acid charcoals, and, indeed, it was shown that the above charcoal of p_{H} 7.9, when extracted with water, filtered off, dried, and re-extracted, gave an extract of p_{H} 5.2. It is probable that the oxalic acid merely displaces the general effect towards the acid end of the scale.

It is well known that preferential ionic adsorption can take place on certain charcoals and on many other types of adsorbent, and indeed one ion may be practically completely adsorbed, the other remaining in solution (Freundlich, "Kapillarchemie," p. 275). Hydrogen ions are especially easily adsorbed, and from, *e.g.*, hydrochloric acid, will be adsorbed more readily than the chloride ions. The selective adsorption cannot reach the true equilibrium for the ion owing to the attraction between ions of opposite charge, chloride ions being adsorbed in amounts greater than, and hydrogen ions in amounts less than, the equilibrium value.

Bohn (*loc. cit.*), in discussing results on the isoelectric point of charcoal, assumes that the surface energy is sufficient to split water into its ions. According to this hypothesis, a negatively charged charcoal would adsorb hydrogen ions preferentially, leaving an excess of hydroxyl ions in solution and thereby giving it a high p_{H} value and making the charcoal positive with respect to it. It has been shown by Kruyt and de Kadt (*Kolloid-Z.*, 1929, 47, 44) that the sign of the charge of sugar charcoal in contact with water, which is normally negative, is reversed on heating in an atmosphere of carbon dioxide to a high temperature, during which process it loses its capacity of adsorbing alkalis. This is in complete accord with the present results.

Frumkin (*ibid.*, 1930, 51, 123), from experiments with platinum-containing charcoals, regards charcoal in aqueous solution as a gas electrode, either a hydrogen or a hydroxyl electrode, the magnitude and nature of acid-alkali adsorption depending on the p_{H} between the charcoal and the solution. It is assumed that hydroxyl ions can be sent into solution from the oxide layer according to the equation $\text{C}_x\text{O} + \text{H}_2\text{O} = \text{C}_x + 2^+ + 2\text{OH}^-$. If this hypothesis is applied to the present results, charcoal would be regarded as functioning as a reversible electrode, either hydrogen or hydroxyl according to the temperature of activation. This may be expressed as follows:—



Although the origin of the hydrogen and hydroxyl ions in charcoal suspensions is obscure, the fact of their existence is important, and the variation of p_{H} with temperature of activation is a fundamental property of charcoal which must be realised before the properties of the surface both as an adsorbent and as a catalyst can be predicted; indeed, it is probably generally more important to know the p_{H} of a sample than its density or adsorptive capacity for dyes, which are often used to indicate its properties.

SUMMARY.

(1) It has been found that the p_H of suspensions of sugar charcoal varies with the temperature of activation of the charcoal.

(2) The surface conditions leading to a constant p_H are established on charcoal when activated for a short time at a low temperature, but not until after 8 hours at high temperatures.

(3) Similar results were obtained with graphite and commercial charcoals; in the latter case the adsorption of acids and bases was shown to vary with the p_H .

(4) The acid condition of the surface due to low-temperature activation was stable, whereas a high-temperature basic charcoal gradually reverted to the acid condition on standing in air.

(5) Carbon dioxide activations gave similar results to those with oxygen.

(6) Reasons for the variation of the p_H of charcoal suspensions with temperature of activation are discussed.

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