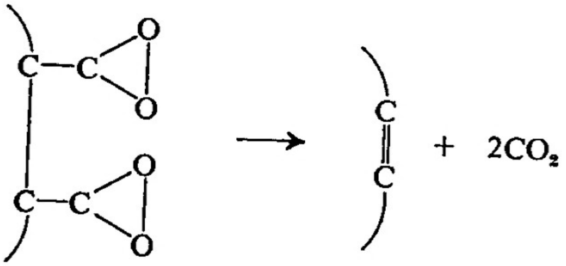
those obtained in aqueous medium. We have also obtained 30–40% higher acidity values for charcoals and carbon blacks using alcoholic potassium hydroxide. It is highly likely that phenols and other weakly acidic structures are completely neutralized only in nonaqueous media.

5. Fixation of oxygen at unsaturated sites

Irreversible adsorption or fixation of bromine from aqueous solution has been taken as evidence of surface unsaturation (*181*). This is rather vaguely supposed to arise either from the presence of quinone groups at sites where they cannot participate in resonance (*159*) or from the presence of olefinic side chains attached to the aromatic nucleus. Some recent work from our laboratory with charcoals (*182*) and with carbon blacks (*183*) has shown, fairly convincingly, that unsaturated sites are caused by the elimination of CO_2 complex. The elimination of the rest of the oxygen as carbon monoxide does not create any unsaturation.

It has also been shown that, generally, one molecule of bromine is fixed for the elimination of two molecules of CO_2 complex (see Table VII). It appears that each molecule of CO_2 complex involves a single adjacent carbon atom, so when two molecules of the complex are eliminated, a double bond is created between the two adjacent carbon atoms. This statement, according to our simple though tentative model of CO_2 complex, may be represented as follows:



It has also been shown (*182*) that it is not only bromine that can be added at these unsaturated sites on treatment with aqueous bromine but also oxygen on treatment with oxidizing solutions such as potassium persulfate in water. In some of the experiments charcoals outgassed at 1200°C were treated first with potassium persulfate solutions of various concentrations and then with 0.1*N* solution of bromine in potassium bromide (2 moles for mole of bromine). The amounts of oxygen and bromine fixed were determined by ultimate analysis. The results (Table VIII) showed that the total of both oxygen and bromine remains almost the same for a given charcoal. It appears, therefore, that oxygen and bromine

TABLE VII

Bromine Fixed by Charcoal and Carbon Black in Relation to CO_2 Complex Eliminated (mEq/100 g)

Description	CO_2 complex	Bromine fixed	Decrease in amount of CO_2 complex on outgassing	Increase in amount of bromine fixed on outgassing
Sugar charcoal original	669	48	—	—
Outgassed at 300°C	359	208	310	160
400°C	206	292	463	244
600°C	48	364	621	316
750°C	Nil	380	669	332
1000°C	Nil	391	669	343
1200°C	Nil	395	669	347
Coconut charcoal original	384	55	—	—
Outgassed at 300°C	314	91	70	36
400°C	59	226	325	171
500°C	8	232	376	177
600°C	Nil	242	384	187
750°C	Nil	248	384	193
1000°C	Nil	244	384	189
Mogul original	137	Nil	—	—
Outgassed at 400°C	83	30	54	30
500°C	45	42	92	42
700°C	18	62	119	62
1000°C	Nil	64	137	64
1200°C	Nil	64	137	64
Mogul-A original	116	Nil	—	—
Outgassed at 400°C	59	27	57	27
500°C	24	48	92	48
700°C	Nil	61	116	61
1000°C	Nil	59	116	59

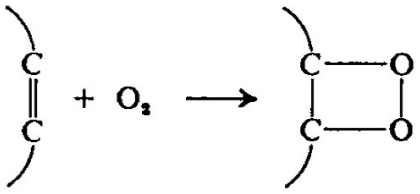
TABLE VIII

Fixation of Oxygen and Bromine on Charcoal Outgassed at 1200°C (mEq/g)

Oxygen chemisorbed	Bromine fixed	Oxygen chemisorbed + bromine fixed
	Sugar charcoal	
0.00	4.14	4.14
1.06	2.68	3.74
1.58	2.12	3.70
2.08	1.78	3.86
2.64	1.16	3.80
	Cotton-stalk charcoal	
0.00	2.30	2.30
0.84	1.18	2.02
1.74	0.38	2.12

are fixed at the same unsaturated sites and that the amount of unsaturation in charcoal is a definite quantity.

The fixation of oxygen at the unsaturated sites has been represented as follows (*184,185*):



The surface-oxygen complex that is formed in this manner has been found to come off as carbon dioxide when evacuated at a high temperature. Unlike the acidic CO_2 complex discussed earlier, however, this oxygen complex is neutral in character (*184,185*). It is also more stable. It starts decomposing in the 500°–600°C temperature range.

Puri and Sharma (*184,185a*) treated a few charcoals and carbon blacks, before and after outgassing them at 700° and 1000°C, with oxygen gas at 400°C and also with a number of oxidizing solutions. It was found that in the original charcoal samples which had not been outgassed and which therefore contained very little unsaturation, the CO_2 complex formed was entirely acidic. That is, the barium hydroxide value remained close to the carbon dioxide evolved in every case. In the outgassed samples, on the other hand, the various treatments gave rise partly to the acidic and partly to the neutral CO_2 complex, as the carbon dioxide evolved was always in excess of the barium hydroxide value.

The results of some of these experiments in the case of sugar charcoal only are given in Table IX. The difference between carbon dioxide evolved and base-adsorption capacity, wherever in excess of 2%, was taken as the amount of neutral complex formed by the addition of oxygen at the unsaturated sites. This view received support from the fact that there was a corresponding decrease in surface unsaturation as measured by bromine value. It is significant to note that the formation of the acidic CO_2 complex, in which two oxygen atoms are assumed to be attached to each active surface carbon atom, does not interfere at all with the bromine value. This shows clearly that the sites involved in this case are entirely different. These sites are probably located at the edges of the basal planes.

The complex formed by the addition of oxygen at the unsaturated sites has been found not only to be neutral, but also to make no contribution towards hydrophobicity or polarity of the surface. This has a transitory existence, however. While studying the distribution of chemisorbed oxygen

TABLE IX

Formation of Acidic and Neutral CO_2 Complex on Various Treatments

Charcoal	Total CO_2 complex, mEq/100 g	Base adsorption capacity, mEq/100 g	Neutral CO_2 complex, mEq/100 g	Bromine fixed, mEq/100 g
Sugar charcoal original	669	665	Nil	45
Treated with $K_2S_2O_8$	975	970	Nil	46
Treated with aq. chlorine	881	902	Nil	41
Treated with H_2O_2	819	810	Nil	44
Treated with acidified $KMnO_4$	675	661	Nil	42
Sugar charcoal, outgassed at 1000°C	Nil	Nil	Nil	398
Treated with $K_2S_2O_8$	144	19	125	278
Treated with aq. chlorine	381	205	176	218
Treated with H_2O_2	331	40	291	110
Treated with acidified $KMnO_4$	175	27	148	215
Coconut charcoal original	391	400	Nil	39
Treated with $K_2S_2O_8$	667	662	Nil	38
Treated with aq. chlorine	709	698	Nil	40
Treated with H_2O_2	578	564	Nil	37
Treated with acidified $KMnO_4$	396	402	Nil	37
Coconut charcoal, outgassed at 1000°C	Nil	Nil	Nil	214
Treated with $K_2S_2O_8$	140	48	92	124
Treated with aq. chlorine	275	149	126	66
Treated with H_2O_2	170	32	138	60
Treated with acidified $KMnO_4$	142	48	94	112

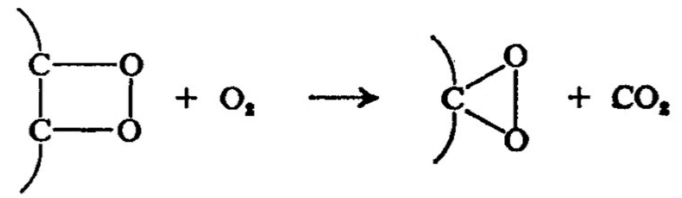
between the two types of CO_2 complexes at different stages of extensive oxidation of sugar charcoal outgassed at 1000°C by oxygen at 400°C or oxidizing solutions, it was observed (*186*) that, at first, most of the oxygen was fixed at the unsaturated sites, giving rise to the neutral complex. As the treatment was continued there was more and more chemisorption of oxygen but the amount of the acidic complex formed at each step was even more than that of the additional oxygen fixed. This showed not only that more oxygen was being fixed as the acidic CO_2 complex, but also that there was progressive conversion of the neutral complex into the acidic complex. Ultimately, the entire CO_2 complex became titratable against alkalies. The results of some of these experiments are reproduced in Table X. The unsaturated sites, however, were not revived with the decrease in the amount of the neutral complex. There was continuous gasification of carbon.

TABLE X

Formation of Acidic and Nonacidic CO_2 Complex at Different Stages of Oxidation of Sugar Charcoal Outgassed at 1000°C

Treatment	CO_2 evolved on outgassing at 1200°C, mEq/100 g	Barium hydroxide neutralized, mEq/100 g	Nontitratable CO_2 complex, mEq/100 g	Percentage of titratable complex	Fixation of bromine, mEq/100 g	Loss in weight, %
No treatment	Nil	Nil	Nil	Nil	398	—
Treatment with oxygen at 400°C for 2 hr at						
92 mm pressure	89	16	73	18	—	—
219 mm pressure	115	36	79	31	—	—
371 mm pressure	179	64	115	36	—	—
525 mm pressure	145	141	4	98	—	—
730 mm pressure	93	91	2	98	—	—
Treatment with hot nitric acid, amount used:						
1 ml/g	265	10	255	4	125	2.5
3 ml/g	317	40	277	13	108	6.0
5 ml/g	396	59	337	15	66	9.8
8 ml/g	445	79	366	18	28	17.4
10 ml/g	560	188	372	34	18	22.5
15 ml/g	869	488	381	57	Nil	—
20 ml/g	1025	780	245	76	Nil	40.8
25 ml/g	1085	995	90	93	Nil	—
30 ml/g	1175	1170	Nil	100	Nil	70.0

The conversion of neutral into acidic CO_2 complex on progressive oxidation, with simultaneous disappearance of unsaturated sites and gasification of carbon, has been represented as follows:



G. Influence of Carbon–Oxygen Surface Complexes on Surface Behavior of Carbons

Whatever be the exact nature and structure of the surface oxides, there is little doubt that the combined oxygen is present mainly at the edges of the giant molecules that constitute the layer planes. As these edges constitute the main adsorbing surface, the oxygen complexes exercise a considerable influence on surface behavior and surface reactions of carbons.

1. Adsorption of electrolytes

The influence on adsorption of electrolytes, in particular acids and bases, has already been discussed in detail. The influence on adsorption of dry ammonia has also been described. Sulfur dioxide is reported (*38*) to be adsorbed so strongly at sites of oxygen complexes that it cannot be recovered until the sample is heated to 220°C. The gas is then liberated as sulfur trioxide.

2. Hydrophobicity

Pure carbon is hydrophobic. The hydrophobicity decreases if oxygen is present. It has long been known that carbon black with a high oxygen content is readily wetted by water. Accordingly, low temperature oxidation of ink, color, and lampblacks is often used to improve their hydrophilic character. Studebaker and Snow (*187*) measured the contact angle (θ) of a number of carbon blacks by a modification of Volkova method (*188*). Cos θ as a measure of wettability was found to be a function of oxygen and hydrogen contents.

3. Sorption of water and methanol vapors

A good deal of work has been reported on the influence of combined oxygen on the sorption of water vapor. The work of Lawson (*189*) and King and Lawson (*128*) shows that the presence of combined oxygen in charcoal increases the low-pressure sorption of water vapor and shifts the isotherms to lower pressures than those that correspond to the same amount of sorption in the absence of any such oxygen. Similar observations were reported by Dubinin and Zaverina (*190*), Healey et al. (*191*), and Anderson and Emmett (*192*).

Pierce, Smith, Wiley, and Cordes (*193*) showed that the water isotherm of Graphon changed materially after exposure to water vapor at 80°C. The difference was attributed to interaction of water vapor with graphon producing a carbon–oxygen surface complex which adsorbed water more readily than the clean carbon surface. They could also increase the amount of water sorbed by Graphon after oxidizing its surface on treatment with water vapor at temperatures varying between 25° and 125°C. It was also observed that while the isotherm on the untreated sample of Graphon was reversible that on the oxidized sample displayed limited hysteresis.

Pierce and Smith (*194*) and Dubinin, Zaverina, and Serpinski (*195*) are of the view that oxygen provides active centers at which sorption of water proceeds in the form of isolated clusters through hydrogen bonds. These clusters then grow in size, as more adsorption takes place on adsorbed water molecules by means of hydrogen bonds, and ultimately they merge at a higher relative vapor pressure, to form a continuous layer in nonporous carbons and to bridge the walls of the pores in porous carbons. The hysteresis arises from the fact that while adsorption proceeds through the formation of clusters, desorption takes place from continuous layers in nonporous carbons, and from meniscii in the case of porous carbons. The forces in the former process are confined to active sites only, whereas in the latter they extend to the whole layer. As a result, this desorption occurs at higher relative vapor pressures.

McDermot and Arnell (*196*) removed oxygen from three types of charcoal by treating them with hydrogen at 1000°C. This resulted in a decrease in water sorption at all humidities below 80 per cent. When the surface was reoxidized by exposing the hydrogen-treated charcoals to water vapor for three months at 60°C, the original capacity to sorb water was largely restored. These authors supported the cluster theory of hystersis.

Puri, Murari, and Singh (*197*) and Puri (*206*) studied adsorption of water at 25°C on charcoal coated with different amounts of oxygen. They showed that it is the oxygen present as CO_2 complex which provides active sites for the sorption of water vapor and that the sorption–desorption isotherms do not meet even at zero relative vapor pressure as long as CO_2 complex is present. This indicated that a certain amount of water sorbed by charcoal containing CO_2 complex could not be desorbed even on evacuating the system to constant weight over sulfuric acid at 25°C. This was regarded as fixed by a mechanism involving hydrogen bonding and was found to correspond roughly to one mole of water for one mole of CO_2 complex. The rest of the combined oxygen was found to have little effect on the sorption of water or the magnitude of hysteresis. A few outgassed samples were treated with nitric acid (*92*) to build a large amount of CO_2 complex. The sorption of water vapor was enhanced throughout the entire range of vapor pressures. The increase in the sorption at 0.38 relative vapor pressure, where there was very little possibility of capillary condensation, corresponded roughly to one mole of water for each mole of CO_2 complex formed. Similar results were obtained in the case of sorption of methanol (*198*). The sorption–desorption isotherms did not meet as long as CO_2 complex was present. The amount of methanol retained by charcoal corresponded roughly to one half mole for each mole of CO_2 complex. The smaller value here was probably due to the larger radius of the nonpolar group in methanol. A methyl group of radius 2 Å adsorbed on an oxygen ion of radius 1.3 Å, lying flat, may block access to the neighboring oxygen ion.

4. Heats of adsorption

The heats of adsorption of ammonia, methylamine, sulfur dioxide, and carbon dioxide, as measured by direct calorimetric techniques, were reported to be high if surface oxygen complexes were present (*199*). Adsorption of water was generally too small to permit direct calorimetric measurements. The isosteric method, based on determination of adsorption isotherms at two different temperatures, yielded conflicting results. This was attributed to small amounts of adsorption, continued reaction of water vapor with the surface which caused increase in surface polarity during the course of sorption measurements, and to the inapplicability of the Clausius-Clapeyron equation under such conditions.

5. Heats of immersion

Heats of immersion of carbon blacks in water and methanol were shown by Kraus (*200*) to be linear functions of oxygen content. In charcoals, however, heats of immersion were reported by Puri, Singh, and Sharma (*201,206*) to vary linearly with respect to combined oxygen evolved as carbon dioxide and not so much with respect to total oxygen (Fig. 9). When the CO_2 complex was increased appreciably on treatment with hot nitric acid (*92*), the heat of wetting of the product increased in direct proportion to the amount of CO_2 complex formed, the increase being about 3 kcal/mole of the complex. This value, incidentally, is of the same order as the heat of dissolution of carbon dioxide in water, that is, 4.78 kcal.

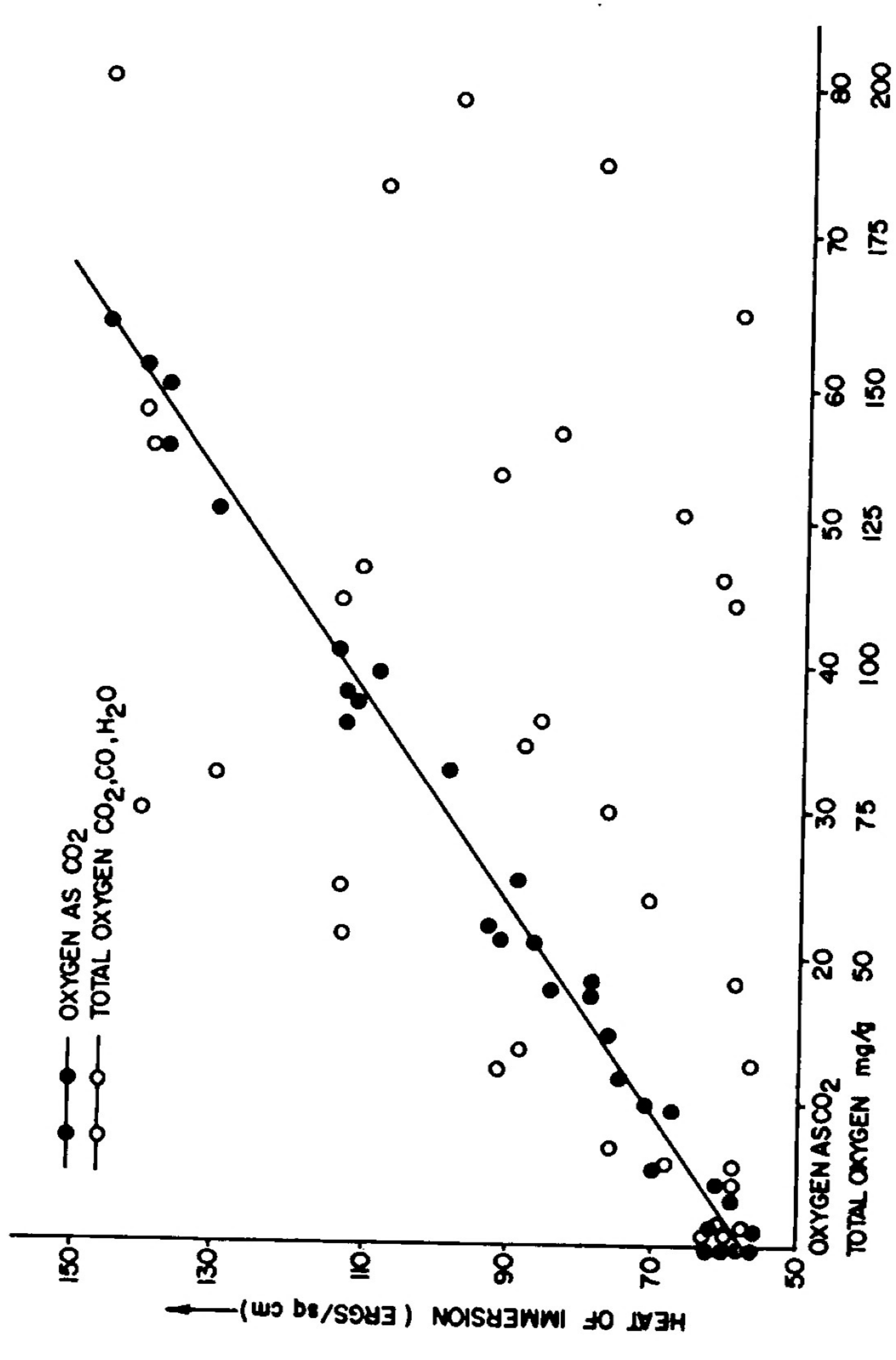


Fig. 9. Heat of immersion of charcoals in relation to chemisorbed oxygen.

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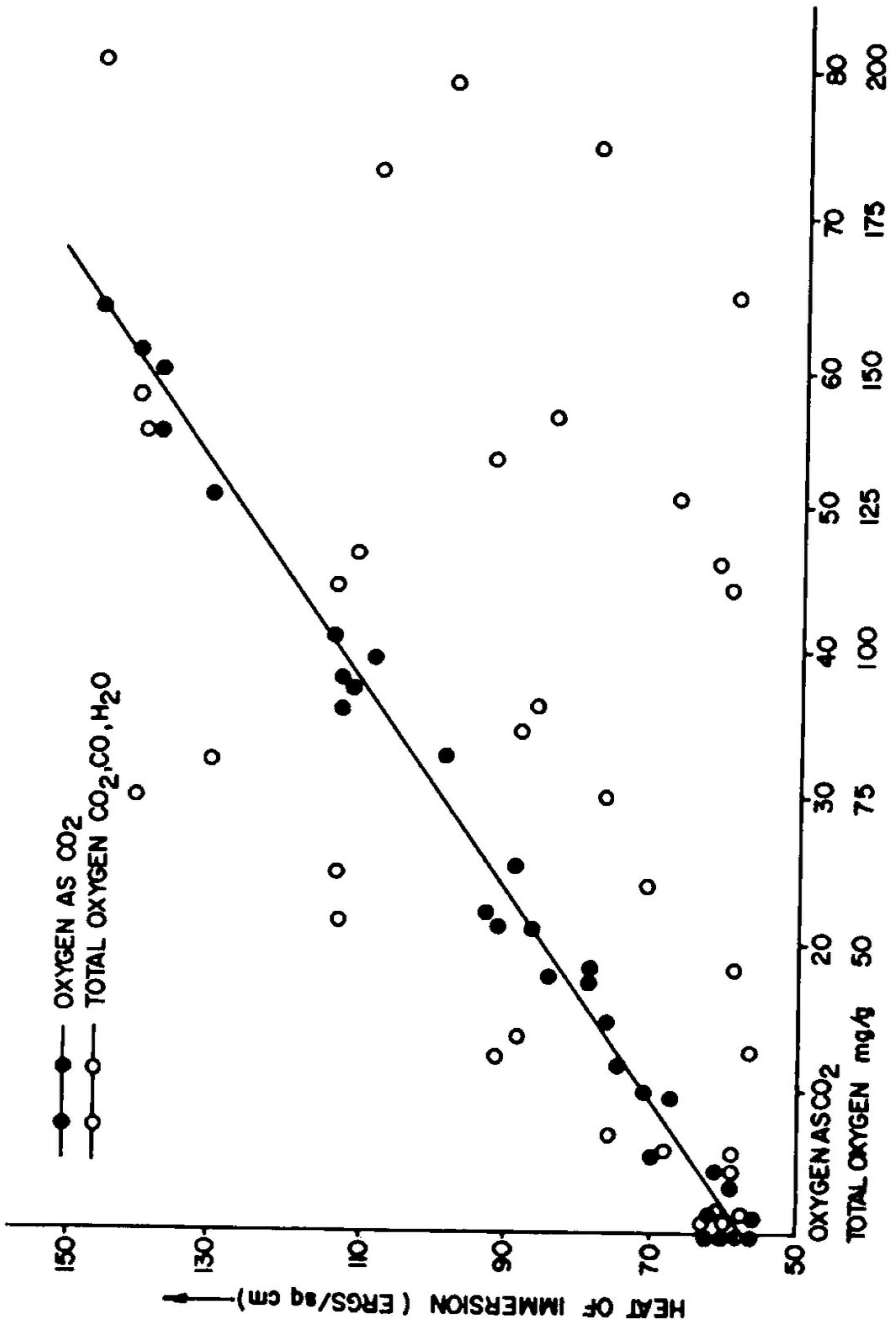

Fig. 9. Heat of immersion of charcoals in relation to chemisorbed oxygen.

6. Selective adsorption

Kipling and co-workers (*202–204*), in their studies of adsorption from binary liquid mixtures, showed that the presence of combined oxygen imparts polar character to carbons, as a result of which they exercise preferential adsorption for a more polar component of a binary mixture. Thus Spheron–6, which contained oxygen, preferred methanol from its solution in benzene, while Graphon, which was essentially free of oxygen, preferred benzene. There were also significant differences with regard to adsorption of benzene from its solutions in heptane. Spheron–6 preferred benzene while Graphon preferred heptane. This behavior was attributed to strong interaction of electrons of the aromatic nucleus with oxygen complexes present on Spheron–6. Puri, Kumar, and Sandle (*205*) and Puri (*206*), working with different samples of charcoal associated with varying amounts of oxygen, showed that the nature of the oxygen complex is even more important than the total oxygen in determining surface interactions of carbons in such cases. The composite adsorption isotherms of ethanol–benzene and methanol–benzene mixtures on the various samples are shown in Fig. 10 and 11 (*205,206*). The concentration axis (abscissa) represents x, the mole fraction of the component in the liquid phase at equilibrium, while the ordinate represents $n_0\Delta x/m$, where Δx is the change in the mole fraction of the same component due to adsorption on m grams of the adsorbent when brought into contact with the binary mixture containing a total of n_0 millimoles. Evidently, the original charcoals, which contained a large amount of CO_2 complex, show great preference

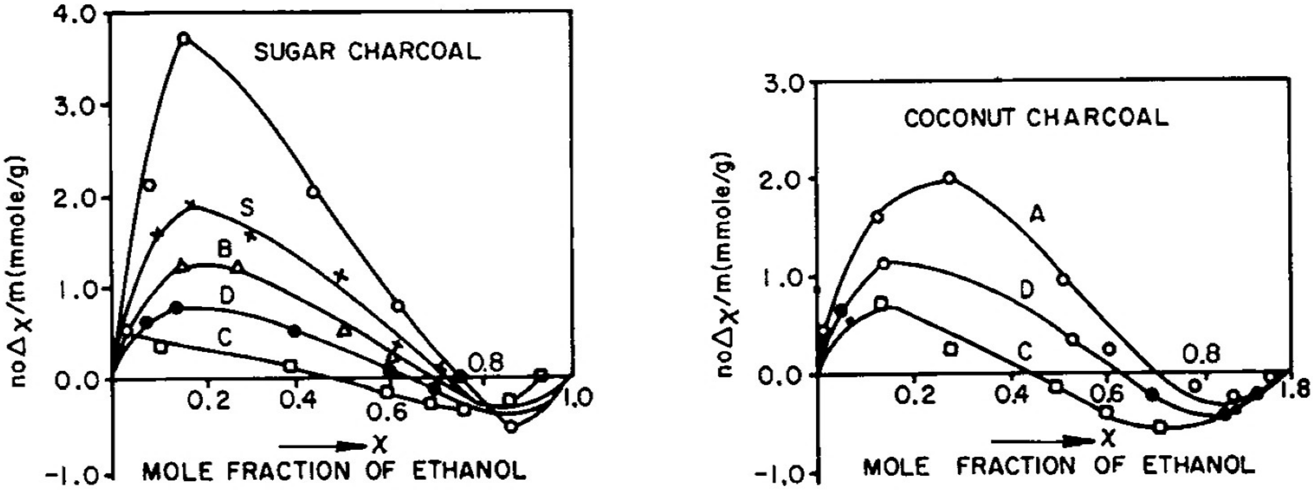

Fig. 10. Composite adsorption isotherms for various samples of charcoal from sugar and coconut shell and silica gel from ethanol–benzene mixtures. Curves A, original charcoals; B, outgassed at 400°C; C, outgassed at 750°C; D, outgassed at 1100°C; S, silica gel.

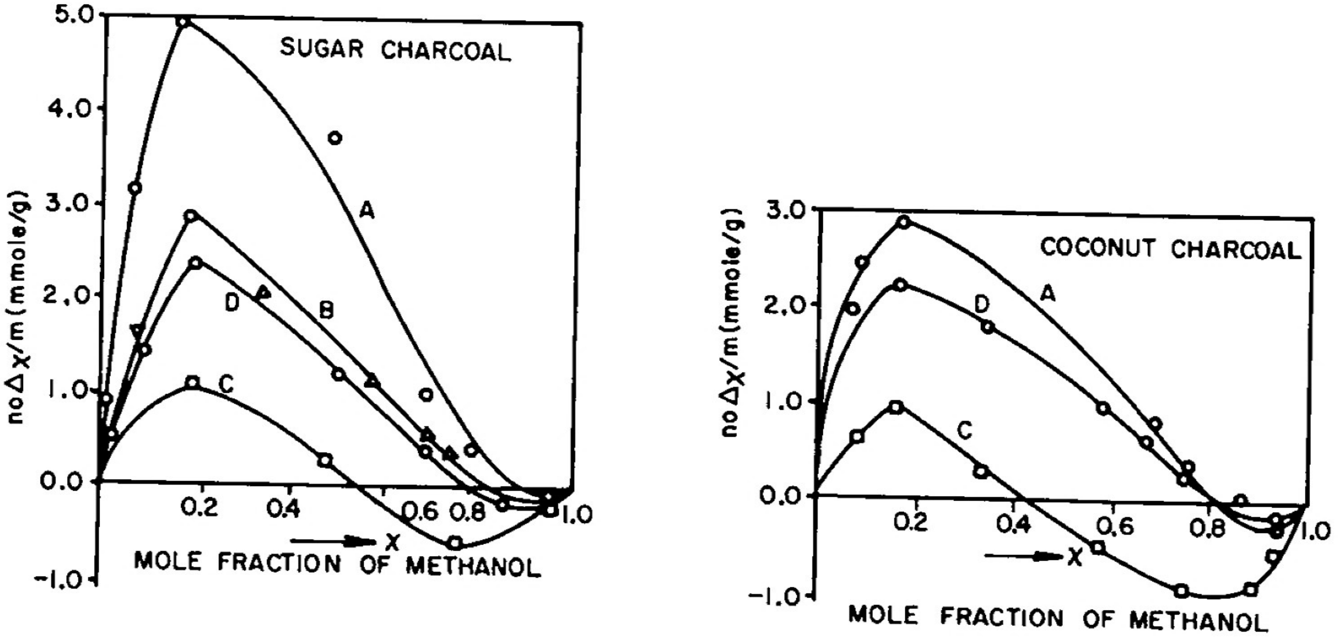

Fig. 11. Composite adsorption isotherms for various samples of charcoal from sugar and coconut shell from methanol–benzene mixtures. Curves A, original charcoals; B, outgassed at 400°C; C, outgassed at 750°C; D, outgassed at 1100°C.

for the polar ethanol or methanol over benzene (see curves A, Figs. 10 and 11). The preference is even more pronounced than that shown by silica gel (curve S, Fig. 10), which is definitely known to have polar groups along its surface.

As part of the CO_2 complex was eliminated on outgassing the charcoals at 400°C, there was an appreciable fall in the preferential adsorption of the alcohols (curves B). When the complex was eliminated completely on outgassing the charcoals at 750°C, there was almost a reversal of the preference (curves C) because then benzene was preferred, though slightly, to ethanol or methanol.

It is interesting to note that the charcoals outgassed at 750°C, retained appreciable amounts of combined oxygen (about 8% in sugar charcoal and 6% in coconut charcoal) that was capable of evolving carbon monoxide. These charcoals show less preference for both ethanol and methanol, and more for benzene, than is shown by the samples outgassed at 1000°C (curves D), which were almost free of oxygen. It appears that quinone groups, which form a part of the CO complex, promote preference for benzene. In this connection mention may be made of the work of Bhacca (*206a*) in which he has discussed the possibility of interaction of electrons of the benzene ring with the partial charge on the carbonyl carbon atom.

Thus while one part of the combined oxygen (present as CO_2 complex) promotes preferential adsorption of alcohols, another part (present as

CO complex) promotes preferential adsorption of benzene. These results indicate the need to determine not only the total oxygen but also the form in which it is evolved in order to assess correctly the performance and surface behavior of carbons.

Recent experiments in the author's laboratories have shown that the oxygen which is fixed at the unsaturated sites on treatment of outgassed charcoals with oxidizing solutions and which is not acidic in character (Cf. Section II.F.5) has little or no effect on sorption of vapors, heats of immersion or selective adsorption of the type mentioned above.

7. Resistivity

Chemisorption of oxygen increases the electrical resistance of carbons. When a thoroughly outgassed powdered carbon was oxidized to about 4% oxygen content on treatment with oxygen in the 500°–700°C temperature range, there was almost a 100-fold increase in electrical resistance (*207*).

8. Catalysis

Because in contact catalysis the reactions take place at the surface of the catalyst, oxygen complexes play significant roles in several reactions catalyzed by carbons. Thus in the case of carbon-catalyzed oxidation in air of $Fe(CN)_6^{4-}$, NO_2^-, AsO_3^-, Sn^{++}, and quinol (*208*), the maximum activity was observed with carbons that contained maximum amounts of oxygen. Similarly catalytic oxidation in air of inorganic anions, including NO_2^-, SO_3^{2-}, AsO_3^{3-}, $Fe(CN)_6^{4-}$, $S_2O_3^{2-}$, and CO_3^{2-}, have been shown to be due to the presence of acidic oxides on carbon surface (*209*). The catalytic activity of carbons for the oxidation of ferrous ions in acid solution by molecular oxygen was found to be about 200 times more in the presence of oxygen-containing groups (*132*).

The rate of auto-oxidation of stannous chloride in an acid solution was maximum in the presence of carbons activated at 550°C which contained oxidized surface (*210*). The catalytic activity for the oxidation of hydroquinone to quinone, on the other hand, was maximum in the presence of carbons activated at 875°C which contained rather small amounts of combined oxygen (*211*).

A good deal of work on the catalytic decomposition of hydrogen peroxide in the presence of activated charcoal has been reported in the literature (*212–216*). The catalytic efficiency has been found to be maximum if charcoal is activated at 850°C and minimum if activated at 400°C (*208*). Brinkmann (*214*) proposed a chain mechanism supposed to be initiated by oxonium hydroxyl groups, while Garten and Weiss (*159*) put forward another mechanism supposed to be initiated by chromene groups. The mechanism of Garten and Weiss provided for the chemisorption of oxygen by the carbons during the reaction, which was reported to take place by Test and Hansen (*213*) in a later publication as well. There was no information, however, regarding the fraction of the total oxygen evolved that was chemisorbed by the catalyst.

The importance of the nature rather than the magnitude of the surface on catalytic activity of carbons was demonstrated by Puri and co-workers (*216,217*). They showed that increase in catalytic activity of carbons with increase in the temperature of heat treatment, as reported in the literature, is due to progressive increase in their surface alkalinity. The charcoals outgassed at 1200°C, which showed distinct alkaline character, were active to the maximum extent. The outgassed coconut charcoal being more basic (pH,9) was more active than sugar charcoal (pH,8) in spite of the smaller surface area of the former. According to these workers, the decomposition of hydrogen peroxide proceeds through its dissociation as a weak acid ($K_a = 2.4 \times 10^{-12}$)

$$H_2O_2 \rightleftharpoons H^+ + OOH^-$$

The OOH^- ion, being even less stable than hydrogen peroxide itself, decomposes very readily, shifting the dissociation reaction more to the right. In an alkaline environment, evidently, the dissociation of hydrogen peroxide would increase and this would render the compound even less stable. The amount of oxygen chemisorbed by the charcoal was found to be only a very small fraction of the total oxygen rendered available during the reaction. It gave rise mostly to acidic CO_2 complex, in the original charcoal and those outgassed at 400°C, and to the nonacidic CO_2 complex in charcoals outgassed at 700°C and 1200°C (see Table XI), which had unsaturated sites suitable for the formation of this type of complex. The catalytic performance of the first two samples, therefore, came to a standstill after some time, while that of the other two continued appreciably for a fairly long time, as shown in Fig. 12.

III. CARBON–HYDROGEN SURFACE COMPLEXES

Besides oxygen, hydrogen is also present, almost invariably, in most of the carbons. This is to be expected because carbons are pyrolyzed residues of organic compounds. The hydrogen is present as chemisorbed water and as phenolic, hydroquinonic, and possibly carboxylic groups. Besides these forms, hydrogen is also present in direct combination with carbon atoms. The latter is held even more firmly than oxygen is, and it comes off

TABLE XI

Chemisorption of Oxygen by Charcoal and Development of Acidity During Decomposition of 3*N* Hydrogen Peroxide

Charcoal	H_2O_2 decomposed in 24 hr at 35°C, mEq/0.2 g	Oxygen chemisorbed and evolved as CO_2 on evacuation, mEq/0.2 g	Increase in base adsorption capacity, mEq/0.2 g
Sugar charcoal			
Original	4.0	0.28	0.26
Outgassed at 400°C	6.7	0.10	0.09
Outgassed at 750°C	22.5	0.08	Nil
Outgassed at 1200°C	26.7	0.64	0.04
Coconut charcoal			
Original	6.0	0.25	0.24
Outgassed at 400°C	9.0	0.09	0.08
Outgassed at 750°C	32.2	0.08	Nil
Outgassed at 1200°C	38.4	0.39	0.02

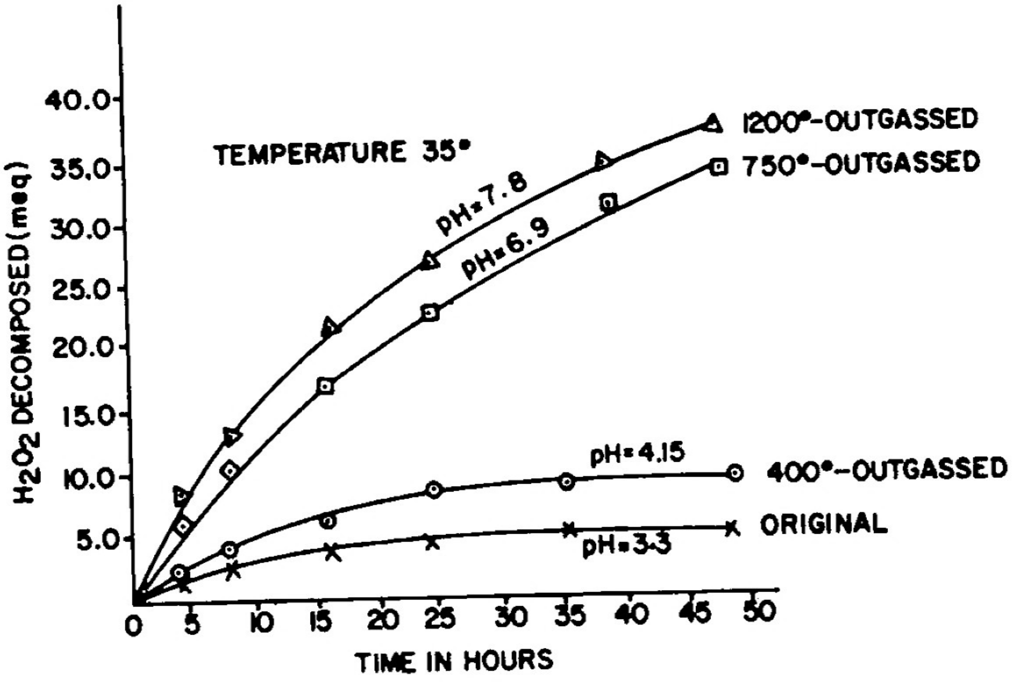

Fig. 12. Catalytic decomposition of hydrogen peroxide at 35°C in presence of different charcoals.

as elementary gas in noticeable amounts only when carbons are outgassed in the temperature range 500°–600°C. It is not eliminated completely even if the temperature of the vacuum is raised to 1200°C.

The total hydrogen content in carbon blacks that have been accurately analyzed (*65*) varies between 0.01% and 0.8%. This quantity, although very small, is important because of the low atomic weight of hydrogen which is only $\frac{1}{12}$th of that of carbon. Each hydrogen atom may bind one mobile electron and therefore the seemingly small amount of hydrogen may have a great influence on the properties of carbon blacks. The electrical resistance of carbon blacks, for instance, increases almost in proportion to their hydrogen contents (*65*).

There has been some speculation regarding the location of hydrogen in the carbon structure. Redmond and Walker (*218*), from the value of isosteric heats of sorption of hydrogen on some selected nuclear and spectroscopic graphites in the temperature range of 1035°–1375°C and over the coverage range of 0.5 to 0.8, concluded that the sorption on carbon atoms occurs at the edges of the crystallites and that there was no significant intercrystalline chemisorption. Studebaker (*65*), by plotting the number of carbon atoms present at the edges of the parallel planes against the number of hydrogen atoms in channel blacks, obtained a nearly straight line. The slope of this line indicated that one hydrogen atom was present for 3.2 carbon atoms present at the edges of the layer planes.

Infrared studies of anthracites of 90–94% carbon content showed (*219*) that the hydrogen is partly aromatic and partly aliphatic and that the aromatic/aliphatic ratio increases markedly with increase in the carbon content. The aliphatic hydrogen is considered to be present in the form of aliphatic chains and alicyclic rings, attached to the periphery of aromatic rings. The aromatic hydrogen is considered to be covalently bonded to the carbon atoms at the periphery of the aromatic platelets.

Treatment of charcoal or carbon black in a current of hydrogen at 1000°C has been used (*63,117,196*) for the removal of oxygen complexes. No carbon–hydrogen complexes are formed during the treatment, however. As a matter of fact, an appreciable portion of the combined hydrogen is eliminated during the process (*117*). Lahiri and co-workers (*220*) have shown that treatment of a low-rank coal with hydrogen at a pressure of 200 atmospheres and 375°C results in the enrichment of the mass with hydrogen. Lobenstein and Deitz (*28*) treated bone char with hydrogen at 200° and 400°C. The treatment at 400°C, but not that at 200°C, enhanced chemisorption of oxygen by the chars on exposure to the gas at 200°C. The treatment in hydrogen at 300°C lowered the hydrogen content of

Spheron-9 slightly (*172*). With increasing temperatures, however, the hydrogen content increased to the maximum value at 500°C and fell again at 600°C and above. Studebaker (*172*), like Smith et al. (*63*), did not notice any change in surface area during treatment in hydrogen at any of the temperatures. Emmett (*67*), however, reported an appreciable increase in surface area together with an appreciable loss of carbon as methane during the treatment. He likened this process to activation processes in steam or carbon dioxide.

A few kinetic studies on the chemisorption of hydrogen have also been reported. Kingmann (*221*) measured the rate of sorption on a Norit G. R. Charcoal and found the rate at 420°–530°C to vary directly as the pressure of the gas and the extent of the available surface. The rate in the first few minutes, however, was always greater than the calculated value. This suggested the presence of a few very active sites where the reaction occurred very rapidly. Barrer (*222*) found the rate of chemisorption of hydrogen on charcoal between 300° and 600°C to depend exponentially on the temperature, and above 600°C to vary with the square root of the temperature. As the latter relationship is characteristic of diffusion, it was concluded that the gas was penetrating into the interior of the adsorbent. Barrer (*222a*) also reported a small though strong chemisorption of hydrogen on diamond and graphite. The rate which was rapid at first slowed down steadily with time. Redmond and Walker (*218*) also studied the kinetics of sorption of hydrogen on graphites of high grade purity and found the rate of desorption over the temperature range of 1035°–1325°C to follow the Elovich equation.

Treatments with chlorine and sulfur at elevated temperatures cause considerable dehydrogenation of carbons.

Puri and Bansal (*223–225*) studied the chlorination of sugar- and coconut charcoals, which contained initially about 3.3 and 2.2% of hydrogen, respectively. They observed that the elimination of hydrogen, which commences generally in noticeable amounts in vacuum only in the 500°–600°C temperature range, takes place appreciably even at 30°C when chlorine is passed. Nearly one-third of the hydrogen was found to be eliminated at 30°C and more than half at 100°C. There was no further elimination on raising the temperature of treatment to 200°C or even 300°C.

The next decrease in the hydrogen content was noticed at 400°C. The values remained unchanged again thereafter and further elimination of the residual hydrogen started only when the temperature reached 900°C. It proceeded nearly to completion at 1200°C. This step-wise elimination of

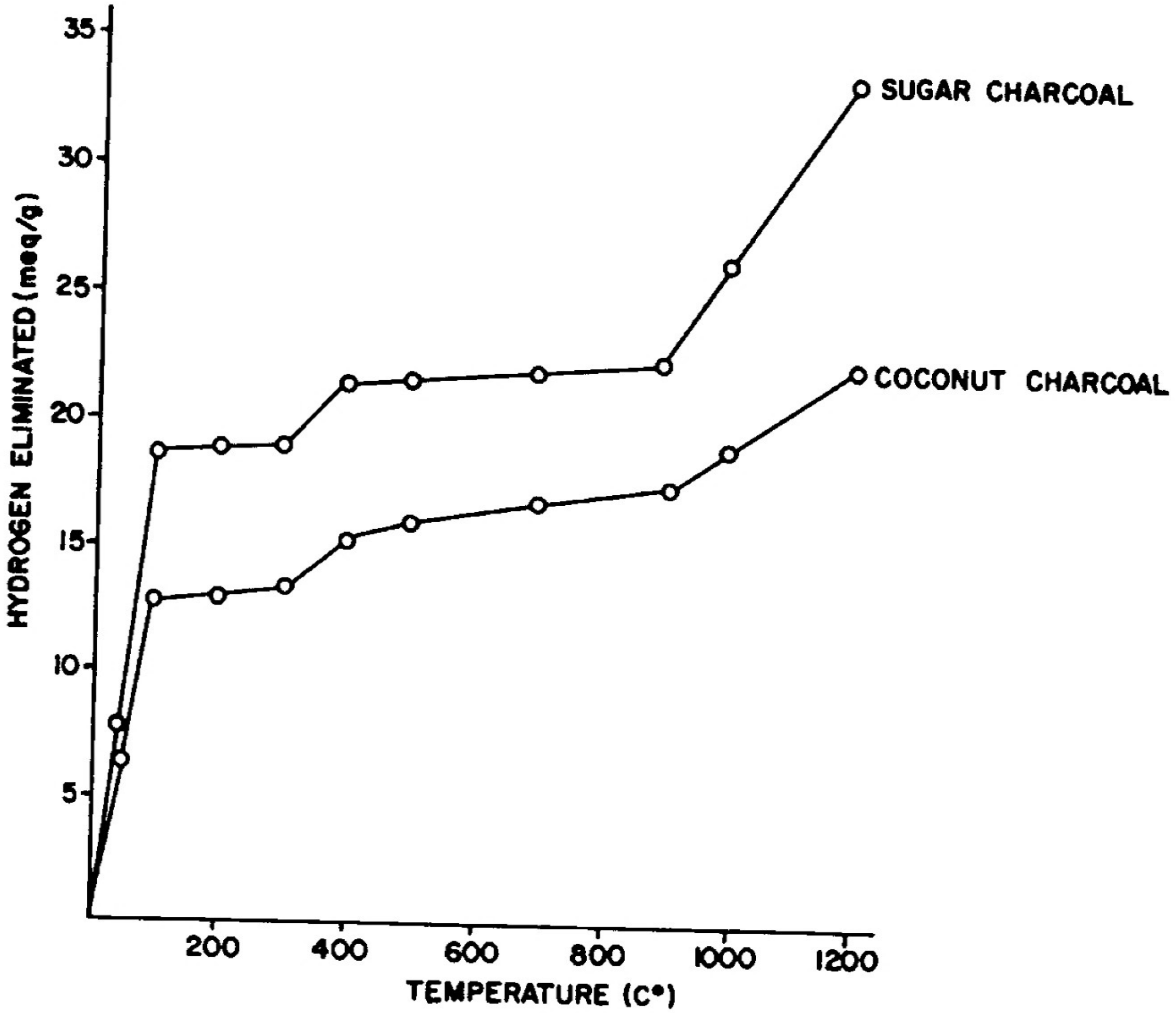

Fig. 13. Effect of treating original sugar and coconut charcoals with chlorine at different temperatures on elimination of hydrogen.

hydrogen from sugar and also from coconut charcoal is shown in Fig. 13. It appears to be significant, as it indicates either that hydrogen is bonded with different energy levels which are not continuous or that only part of the hydrogen is present at the surface and the rest of it is dispersed in more than one layer in the interior of the particles.

IV. CARBON–NITROGEN SURFACE COMPLEXES

Nitrogen is present in some of the carbon blacks but the quantities are not considered to be significant. The affinity of carbon blacks for nitrogen is evident from the fact that the nitrogen content of a carbon black is increased during the curing of mixtures (*65*) of carbon black with natural rubber. This is taken as due to the removal of proteins or protein degradation products from the rubber by the carbon black.

A number of investigations on reactions of charcoals and carbon blacks with nitrogen compounds, in particular ammonia and amines, have been reported. The presence of surface-oxygen complexes is known to enhance the magnitude of such reactions, as was discussed at some length in Section IIF. An outgassed charcoal essentially free of oxygen was shown (*67*) to fix an appreciable amount of nitrogen on treatment with ammonia at 750°C and also at 900°C. The hydrogen content of the charcoal was found to increase from 15.6 to 30.5 and 39.3 mEq/g after treatment in ammonia at 750° and 900°C, respectively. The carbon–nitrogen complex was found to be highly stable. Nitrogen could be recovered only on heating in the 900°–1200°C range, mostly free nitrogen, and slightly as hydrogen cyanide, cyanogen and ammonia.

Wibaut (*226*) heated some of his carbons in a stream of ammonia at 300°C for three hours. This was followed by flushing with nitrogen at the same temperature for one hour and then cooling in a stream of nitrogen. It was found that while no nitrogen was fixed by Ceylon graphite and diamond powder, 2.5% of nitrogen was fixed by activated charcoal. This nitrogen could be split off as ammonia on treatment with hydrogen, from which it was inferred that nitrogen was not fixed in a heterocyclic ring structure but was probably present in the form of a nitrile group.

Studebaker (*65*), after heating a number of carbon blacks with dimethylamine at 150°C in an unsealed Carius tube in a steel bomb for an hour, found an appreciable fixation of nitrogen in every case, the amount increasing with increase in the initial oxygen content of the sample. Further, it was found that the number of atoms of nitrogen fixed was approximately equal to the sum of the 1,4-quinone type of oxygen, as determined by catalytic hydrogenation, and the active hydrogen, as measured by Grignard reagent. This implied that nitrogen was fixed by interaction with quinonic as well as phenolic and carboxylic groups.

Hofmann and Ohlerich (*156*) heated a sugar charcoal, which had been given prolonged treatment with a mixture of nitric acid and sulfuric acid at 80°C and contained 16.6% of oxygen, with well-dried ammonia for 10–20 hr at temperatures lying between 110° and 410°C. The treated carbon was then outgassed for six hours in vacuum at the temperature of the treatment. Although there was no fall of hydrogen—in fact the hydrogen content increased with increase in temperature up to a maximum of 400°C—one atom of nitrogen was introduced for every two atoms of oxygen removed. The analysis of the products showed (*172*) that an O/N ratio which was more than 1 at relatively lower temperatures dropped close to 1 at 300°C or above. This indicated that treatment at lower temperatures produced the ammonium salt of the acid surface oxides and that at high temperatures water was split off, resulting in the formation of acid amide with the ratio close to 1. As these workers rightly pointed out, however, there was no significant evidence to establish the nature of the nitrogen-containing group. Studebaker (*172*), on reacting Philblack–0 and Spheron–9 with dry ammonia at 300°C for 24 hr (by following essentially the same procedure as had been followed by Hofmann and Ohlerich), found that while the ratio O/N in Philblack–0 was 0.93, i.e., close to 1, it was 1.65 for Spheron–9. It was concluded, therefore, that fixation of nitrogen by carbons depends on the nature of the oxygen-containing groups initially present on the surface. The nitrogen was bonded so firmly that only a small fraction could be recovered on heating with concentrated sodium hydroxide or hydrochloric acid at 300°C, which showed great stability of the surface complex formed.

The work of Puri and Mahajan (*171*) indicates that reaction of charcoal with dry ammonia is of two types, one of which involves neutralization of the surface acidic complex. The adsorbed ammonia here can be recovered completely on hydrolysis with hot sodium hydroxide or hydrochloric acid. The second type of reaction results in fixation of ammonia in nonhydrolyzable form and it has not been possible so far to put forward any satisfactory explanation for this or attribute it to any specific group on the carbon surface. This reaction seems to be of activated type, as the amount of nitrogen fixed has been found to increase with increase in the temperature of the treatment up to 400°C (see Table II). Puri and Satija (*227*) have offered evidence to show that nonhydrolyzable nitrogen fixed by carbon blacks on treatment with ammonia at 400°C varies with quinonic oxygen as well as with surface area.

V. CARBON–HALOGEN SURFACE COMPLEXES

The work reported on carbon–halogen systems so far is far less than that on carbon–oxygen systems. Marsh et al. (*228*) in 1929, however, and Eocles et al. (*229*) in 1931 reported that during chlorination of coals at elevated temperatures, there is not only evolution of hydrogen chloride (the amount depending upon the hydrogen content of the coal) but also fixation of appreciable amounts of chlorine. Ruff (*230*) in 1935 reported similar findings on chlorination of charcoals and carbon blacks. Only a small fraction of the combined chlorine could be pumped out by cooling or by the action of boiling with 10% sodium hydroxide.

Reyerson and Wishart (*231*) and Reyerson and Cameron (*232,233*), from a study of the adsorption isotherms of chlorine, bromine, and iodine on activated charcoal and silica gel at 31.6° and 91.5°C, found that whereas the adsorption on silica gel was reversible that on charcoal was irreversible. The adsorbed chlorine could not be recovered even by prolonged evacuation at 600°C. Alekseeviskii and Likharev (*234*) activated a wide variety of charcoals in chlorine at 750° and 950°C. The products, though superior to commercially available materials, had accumulated an appreciable amount of chlorine which could not be eliminated by boiling with alkali, or heating in vacuum, or by electrodialysis. This again indicated high stability of the carbon–chlorine complex formed. The amount of chlorine in the complex varied with the nature of the charcoal as well as with the temperature of treatment. Emmett (*67*) reported fixation of 17% chlorine on treatment of charcoal with the gas at 400°C. It could not be eliminated even after evacuation for an extended period at the same temperature. The exact manner of this fixation was not understood. There was no evidence, however, of any change in available surface area as the adsorption of nitrogen at 0.99 relative pressure remained about the same.

Pinchin (*235*) reported formation of a stable carbon–chlorine complex containing up to 24% of chlorine on treatment of coals with chlorine at 1100°C. Boehm, Hofmann, and Clauss (*151*) reported fixation of chlorine by carbon blacks on treatment with the gas in the 400°–500°C temperature range, which resulted in the formation of a stable complex. The amount of chlorine so bound was roughly equivalent to the initial hydrogen content of the carbon black before chlorination. This suggested substitution of hydrogen by chlorine. The chlorinated sample still retained an appreciable amount of hydrogen which was attributed to the presence of moisture. The chlorine in the chlorinated samples was available for reactions with dry ammonia at elevated temperatures as well as with potassium hydroxide and sodium cyanide on fusion.

Rivin and Aron (*236*) treated a few carbon blacks with chlorine, bromine, and iodine in the gaseous phase at different temperatures between 0° and 100°C, as well as in the solution phase at the room temperature. They found appreciable fixation of the halogens, giving rise to stable carbon–halogen surface compounds. The reactivity of the halogens was found to decrease in the order Cl > Br > I. The stability of the complex also varied in the same order. Thus while the whole of the combined iodine was dissociated, only 80% of the bromine and 60% of the chlorine was dissociated in the presence of suitable nucleophiles.

Puri, Malhotra, and Bansal (*224,225*) studied chlorination of a few charcoals outgassed at different temperatures and therefore associated with varying amounts of combined oxygen and hydrogen, at temperatures varying from 35° to 600°C. The reaction involved formation of hydrogen chloride and fixation of chlorine, the former being generally in excess of the latter. The magnitude of each reaction increased with temperature up to 450°C and with time up to 6 hr. The kinetics of the reaction in the current of chlorine approximated those of a reaction of the first order. The maximum of 24% of chlorine by weight was fixed by the original sugar charcoal, and about 40% by the original coconut charcoal. These amounts decreased considerably as the charcoals were outgassed at increasing temperatures and fell to about 10% and 12%, respectively, as the charcoals were outgassed at 1000°C. The decrease in the fixation of chlorine was shown to be due more to a decrease in the hydrogen content than to a fall in the oxygen content of the charcoal.

The relationship between the amount of chlorine fixed at the optimum temperature and the initial hydrogen content of charcoal is shown in Fig. 14 for sugar and also for coconut charcoal. The amount of chlorine fixed for the same amount of hydrogen is seen to be much more in coconut than in sugar charcoal. The difference may be due either to a difference in the nature of carbon–hydrogen bonding in the two varieties of charcoal or, more probably, to a difference in the porosity of the samples so that hydrogen contained in minute capillary pores is more accessible to chlorine in one charcoal than in the other.

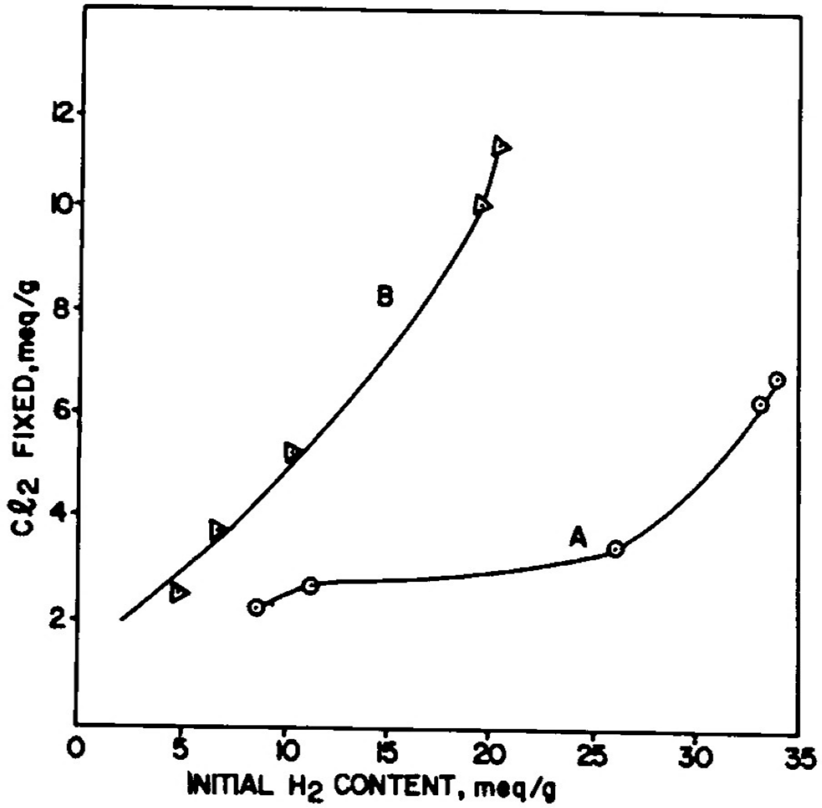

Fig. 14. Relationship between amount of chlorine fixed and the initial hydrogen content of (A) sugar charcoal and (B) coconut shell charcoal.

Although only a part of the hydrogen in charcoal could be substituted for chlorine, the hydrogen content of charcoal influenced the fixation of chlorine to an appreciable extent. It was suggested (*237*) that the hydrogen atoms which are eliminated during the chlorination treatment produce atomic chlorine by the mechanism

$$H + Cl_2 = HCl + Cl$$

and that this facilitates the fixation of chlorine on the various sites. This view was substantiated by a study of the chlorination of toluene in the presence of charcoal samples containing different amounts of combined hydrogen. For this purpose, the hydrocarbon vapor and chlorine were led over charcoal (2 g) heated to 300°C at a flow rate of 3 l/hr. No chlorine derivative was obtained in the absence of charcoal. In the presence of charcoal, there was appreciable conversion of toluene into chlorotoluene, benzyl chloride and benzal chloride. The amount of the conversion decreased appreciably with decrease in the hydrogen content of the charcoal. For instance, original sugar and coconut charcoals which contained 3.4 and 2.0% of hydrogen, caused 22 and 18% halogenation, respectively. When charcoals were outgassed at 1200°C to lower the hydrogen content to 1% or less, the percentage halogenation decreased to about 6 and 4% respectively.

Carbon–chlorine complexes have been found to be highly stable. The combined chlorine could not be recovered by washing with dilute alkali (*67,230*), as already mentioned. A small fraction of it, however, passed into solution as chloride ion when the product was refluxed with 2.5*N* NaOH for several hours (*225*). This fraction probably represents the amount of chlorine fixed by the substitution of aliphatic hydrogen. By heating the product in vacuum at 1000°–1200°C, chlorine was recovered as hydrogen chloride provided a sufficient amount of hydrogen was present. In the case of charcoals deficient in hydrogen (e.g., sugar and coconut charcoals, outgassed at 1000°C before chlorination) most of the combined chlorine was found to remain intact even after evacuation at 1200°C (*225*). The entire amount of chlorine could be eliminated completely on heating the product in a current of hydrogen at 700°C for 8 hr. No free chlorine was detected among the gases evolved.

Treatment of the original charcoals in chlorine at 450°C resulted in the fixation of appreciable amounts of chlorine and elimination of a part of the combined hydrogen as hydrogen chloride, as already mentioned. The chlorinated product, when heated in vacuum at 1000°C, lost almost the entire chlorine as hydrogen chloride. The residual product was found to be almost free not only of chlorine but also of hydrogen and oxygen (*225*). This observation, incidentally, places at our disposal a convenient method of eliminating hydrogen from charcoals. Ordinarily, this requires heating in vacuum at temperatures above 1600°C, where considerable graphitization and loss of surface is known to take place.

Puri and Bansal (*237*), taking the bromine value as a measure of surface unsaturation, showed that fixation of chlorine takes place partly by addition at the unsaturated sites created by eliminating the CO_2 complex (*182,183*) and partly by the substitution of combined hydrogen. As unsaturated sites are few in carbon blacks as well as in original charcoals which have not been outgassed, the bulk of the chlorine is fixed by substitution of hydrogen, as had been observed by Boehm et al. (*151*). In outgassed charcoals, however, as the hydrogen content falls and unsaturated sites are created, fixation of chlorine takes place more by the addition process and less by the substitution process. All the hydrogen in a charcoal cannot be substituted for chlorine. For example, in charcoals outgassed at 1000°C or 1200°C, although there was an appreciable amount of residual hydrogen, fixation of chlorine was almost entirely by addition at the unsaturated sites. There was little or no substitution of hydrogen, although it came off substantially either as hydrogen chloride or as elementary gas during the chlorination. It appears that hydrogen sites in these cases are held in extremely fine capillary pores which are not accessible to chlorine. There was relatively greater substitution of hydrogen in coconut charcoal than in sugar charcoal, presumably because of the relatively coarser capillary structure of the former. Also there was almost complete substitution in carbon black, because of their essentially nonporous structure.

The work of Walker and co-workers (*219*) on chlorination of anthracites with high and medium contents of volatile matter and carbon blacks low in volatile matter at temperatures between 200° and 1400°C has offered support to some of the views expressed and has extended them further. It has been shown that if the content of volatile matter is high fixation occurs primarily by substitution of chlorine for hydrogen in aliphatic groups if the temperature of the treatment is low, and at the edges of the aromatic platelets if the temperature of the treatment is high. For coals with medium content of volatile matter, fixation at all temperatures is by substitution of chlorine for hydrogen at the edges of the aromatic platelets and by addition at the new active, presumably unsaturated, sites created by elimination of the oxides of carbon from the edges of the aromatic