platelets. In carbon blacks low in volatile matter there was very little fixation of chlorine.

The formation of a chlorine complex on diamond was reported by Boehm (*238*). The diamond–chlorine bond was found to be resistant to hydrolysis by hot aqueous sodium hydroxide.

As the optimum temperature for maximum fixation of chlorine and also oxygen is close to 400°C, Puri and Sandle (*239*) studied the simultaneous chemisorption of both on treatment with oxygen–chlorine mixtures of different relative proportions at this temperature. The two gases were found to compete with each other for fixation at the unsaturated sites, and the gas with the greater partial pressure in the mixture was fixed to a larger extent. When the two gases were in equal proportions, oxygen was fixed to a larger extent than chlorine. Apart from these common sites there were other separate sites for fixation of oxygen and chlorine independently of each other. These sites, for the fixation of oxygen, were provided by certain active centers where formation of acidic CO_2 complex and quinonic or phenolic groups etc. was possible and, for the fixation of chlorine, by those centers where substitution of chlorine for hydrogen was possible. Simultaneous chemisorption of oxygen and chlorine by repeated treatments with chlorine water (*240*) and with H_2O_2–HCl mixtures at room temperatures (*241*), with more or less similar conclusions, were reported by Puri and Sehgal.

Reactions of charcoals and carbon blacks with bromine vapor was studied at different temperatures in the same way as with chlorine by Puri and Sehgal (*242*). There was formation of hydrogen bromide and irreversible fixation of bromine giving a stable carbon–bromine complex. The optimum temperature was found to be close to 500°C, 8 hr treatment was found to be sufficient for attainment of the end point. The magnitude of the reaction was less than that with chlorine under similar conditions of treatment. As the bromine atom is heavier, however, the amount of bromine fixed by weight was higher than that of chlorine under similar conditions. The maximum amount of bromine in the complex was 38% in the original charcoal and 31% in Spheron–9. The amount of hydrogen bromide was considerably in excess of bromine fixed in charcoals, showing that all the hydrogen eliminated during the bromination was not substituted by bromine, evidently because of the inaccessibility of some of the sites located within the minute capillary pores of the charcoal. In nonporous carbon blacks, however, the amount of hydrogen bromide formed was fairly close to the amount of bromine fixed, indicating more or less complete substitution of hydrogen by bromine.

Fixation of bromine by the treating of charcoals (*182*) or carbon blacks (*183*) with aqueous bromine has been found to take place only at the unsaturated sites. This, in fact, has been taken as a measure of surface unsaturation as discussed in Section II. Fixation of bromine on treatment with vapor (*242*), however, has been found to take place partly by substitution for hydrogen as well.

The carbon–bromine complex has been found to be highly stable, although a relatively larger proportion of the combined bromine than that of combined chlorine has been found to pass into solution as bromide ion when the product is heated with concentrated sodium hydroxide (*225*,*242a*). On evacuating at 1000°–1200°C, the bromine comes off largely as hydrogen bromide, provided a sufficient amount of hydrogen is available; otherwise it stays intact.

Adsorption of iodine on charcoal and carbon black has been investigated mostly from aqueous or nonaqueous solutions and has been found to be largely of a reversible type. The importance of measuring iodine adsorption under fixed conditions, such as pre-treatment of the adsorbent, initial concentration and quantity of the iodine solution used, ratio of KI/I^- in the aqueous solution, time of contact, etc., was rightly emphasized by Koide et al. (*243*). Smith et al. (*244*), King (*245*), and Linner and Williams (*246*) attempted to correlate iodine adsorption with surface area of the adsorbent, assuming that it is independent of the nature of the surface. Watson and Perkins (*247*) and Razouk and Shimni (*248*), however, could not confirm these conclusions. Puri and Singh (*249*) showed that the amount of iodine recovered from aqueous solution by charcoal under a given set of conditions is influenced considerably by the nature of the charcoal surface. If the surface is acidic, an appreciable fraction of the iodine removed is hydrolyzed into hydriodic acid, and the corresponding amount of oxygen is chemisorbed by the charcoal. Accordingly, iodine adsorption cannot be used for estimating surface areas of charcoals.

Adsorption of iodine from aqueous solution by active carbons and carbon blacks has also been investigated by Hassler and McMinn (*250*), and by Hill and Marsh (*251*). The latter workers concluded that adsorption occurs by filling pores in activated carbons and by multilayer formation in carbon blacks in the same way as adsorption of carbon dioxide at 195°K and nitrogen at 77°K. Puri and Bansal (*252*) have shown that in carbon blacks iodine adsorption measured under standard conditions can serve as an index of the BET nitrogen surface area. Their procedure consists in placing 1 g of carbon black in contact with 100 ml of a solution of 0.15*M* iodine in 2.1*M* KI for a period of 72 hr. About the same value was obtained by allowing the carbon blacks to remain in contact with 0.3*N* solution in benzene or chloroform for 20 days.

Adsorption of iodine from the vapor phase has been shown to have different trends. Puri and Sehgal (*253*) found an appreciable irreversible adsorption of iodine on passing the vapor over charcoal at different temperatures, the optimum temperature being close to 300°C. Most of the iodine was found to be fixed at the unsaturated sites. Connar, Lewis, and Thomas (*254*) studied adsorption of iodine over the pressure range of 0.3–500 mm Hg on reactor grade graphite in the temperature range of 85°–400°C, and desorption from the same specimens at temperatures up to 700°C. The results indicated chemisorption of iodine at temperatures

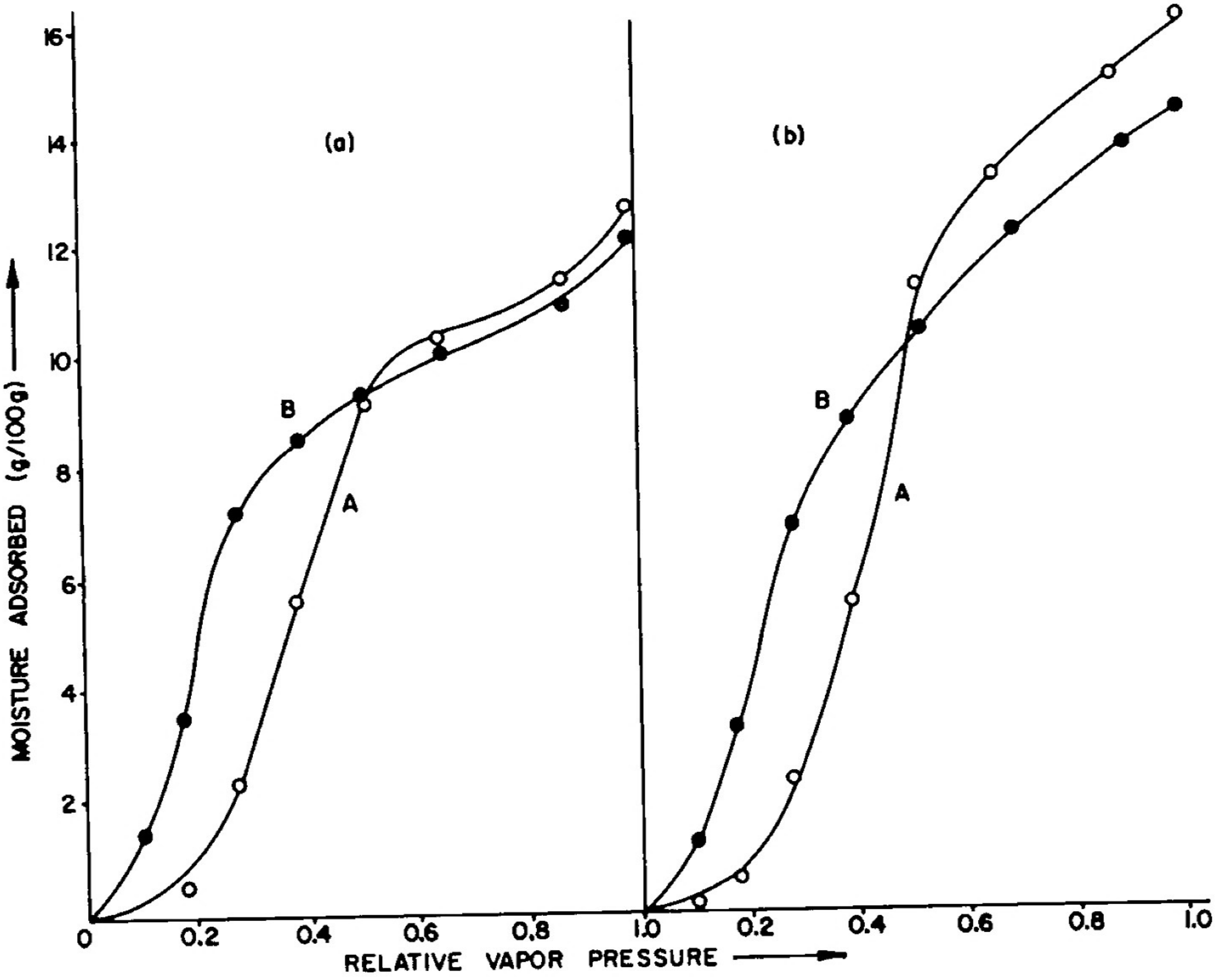


Fig. 15. Water isotherms of sugar charcoal outgassed at (a) 700°C and (b) 1200°C, (A) before and (B) after fixation of bromine.

equal to or above 200°C, but no interlameller compound was formed. The rate of chemisorption followed the Elovich equation.

Unsaturated sites involved in the fixation of halogens, as mentioned previously, have been found by Puri and Kalra (*255*) to play a significant role in catalytic combination of hydrogen and bromine as well as that of hydrogen and iodine, yielding hydrogen bromide and hydrogen iodide, respectively. It appears that both the reactants, e.g., hydrogen and bromine in the hydrogen–bromine reaction, are chemisorbed at the unsaturated sites and then, being held in close proximity to each other, combine to give hydrogen bromide which is readily desorbed. This makes the sites available again for the chemisorption of the reactants. The hydrogen–bromine and hydrogen–iodine reactions, which are endothermic and have high activation energies, ordinarily take place only at high temperatures. They take place quantitatively, however, and to completion even at 150°C in the presence of charcoal that contains unsaturated sites. The catalytic performance of the charcoal ceases if the unsaturated sites are already occupied by oxygen, sulfur, etc.

Fixation of chlorine results in increasing sorption of water by charcoal (*256*) and by carbon black (*257*) at lower relative vapor pressures but it decreases at higher relative vapor pressures. This indicates alteration in sizes of pores but this may also be due to heat treatment during the chlorination process.

Figure 15 shows the effect of fixation of bromine on water isotherms at 25°C when charcoal was treated with *aqueous* bromine at ordinary temperatures in which there was no side effect of heat treatment (*182*). The treated samples pick up considerably more moisture up to 50% relative humidity and slightly less thereafter. The curves for the treated and untreated samples intersect at 50% relative humidity. These observations indicate a considerable narrowing down of the capillary pores as a result of the fixation of bromine. The enhanced water sorption at lower humidities appears to be due partly to narrowing down of capillary pores and partly to a decrease in hydrophobic (or increase in hydrophilic) character. This was also indicated by an appreciable increase in the heat of wetting the charcoal in water after fixation of bromine (see Table XII).

The effect of fixation of bromine on carbon blacks, which are essentially nonporous, on water isotherms (Fig. 16) (*183*) is seen to be of a different kind. The complete isotherms are seen to shift upward, after fixation of bromine, and there is a uniform increase, more or less, in all ranges of vapor pressure.

TABLE XII

Heats of Immersion of Charcoals and Carbon Blacks in Water in Relation to Bromine Fixed

Sample	Bromine fixed, mEq/100 g	Heat of immersion in water, cal/100 g
Sugar charcoal outgassed at 700°C		
Before bromination	Nil	387
After bromination	415	775
Sugar charcoal outgassed at 1200°C		
Before bromination	Nil	368
After bromination	415	734
Philblack–A		
Before bromination	Nil	83
After bromination	30	98
Philblack–O		
Before bromination	Nil	195
After bromination	40	215
Spheron–6		
Before bromination	Nil	196
After bromination	62	226
Spheron–C		
Before bromination	Nil	306
After bromination	70	342

VI. CARBON–SULFUR SOLID COMPLEXES

Sulfur, like oxygen, hydrogen, and nitrogen, is almost invariably present in coals. The fraction which is present as free sulfur, or in combination with metals, is called inorganic sulfur while the rest of it is known as organic sulfur. This element is also present in carbon blacks in amounts varying from zero to over 1% (*258,259*), depending upon the sulfur content of the feed stock. Apparently all of it is chemically bonded with the carbon.

Carbon–sulfur solid complexes of high stability and nonstoichiometric composition can be formed by heating a variety of chars, activated carbons, or carbon blacks with sulfurous gases and vapors. The reactions involved are essentially heterogeneous in which both the nature and the magnitude of the surface are of primary importance. Wibaut (*226*,

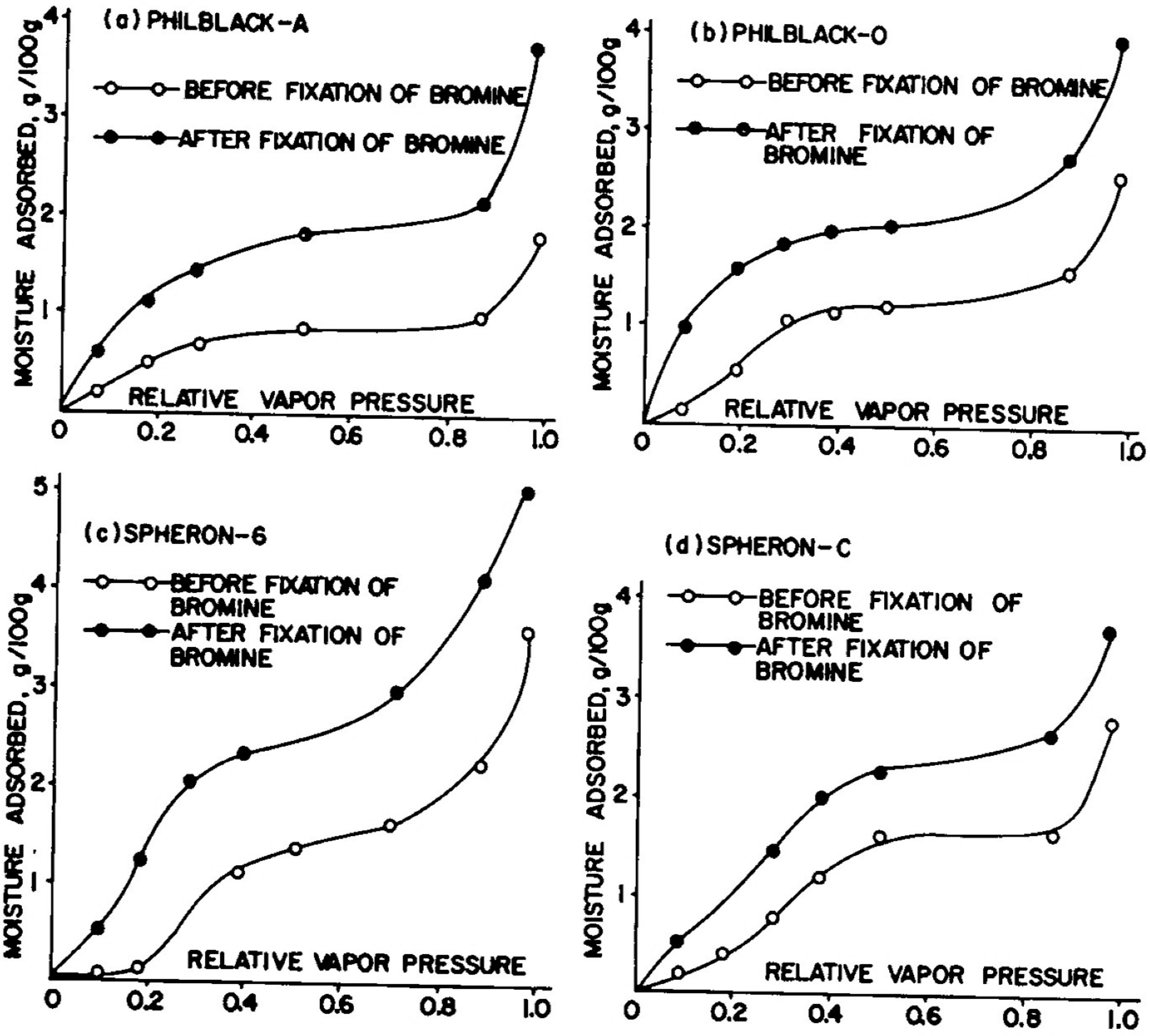


Fig. 16. Water isotherms of carbon blacks before and after fixation of bromine.

260–263) in the 1920's and 1930's heated various types of carbons with sulfur at temperatures varying from 100° to 1000°C and found maximum chemisorption of sulfur, varying between 18 and 25%, depending upon the nature of the carbon at 600°C. Small amounts of hydrogen sulfide and carbon disulfide were also formed during the treatment. The combined sulfur could not be recovered even by repeated extractions with carbon disulfide or with boiling toluene. When the products were heated in vacuum at 1000°–1100°C, however, it came off as elementary sulfur and carbon disulfide; and when heated in hydrogen at 700°C, it came off as hydrogen sulfide. Juza and Blanke (*264*) studied the reaction of sulfur with charcoals, carbon blacks, and graphite between 100° and 1000°C at various pressures. The fixation of sulfur, according to them, was due to capillary condensation, adsorption, chemisorption, and solution in the carbon structure.

Medvedev and Petropolskaye (*265*) and Lewis and Metzner (*266*) found that treatment of coals with sulfur at 350°C caused fixation of sulfur and considerable dehydrogenation of coal with the evolution of hydrogen sulfide. Mazumdar et al. (*267,268*) believed that the evolution of hydrogen sulfide was due to the interaction of sulfur with alicyclic structures present in coals. The possibility of selective dehydrogenation of alicyclic structures by sulfur was considered to be remote by Iyenger et al. (*269*). Young and co-workers (*270*) heated a number of samples of charcoal with sulfur at 400°C in a rotating furnace. About 41% of the sulfur, which was reduced to about 29% by extraction with solvents, was incorporated in the charcoal. The hydrogen content decreased to about one-third of the original value. The combined sulfur decreased the porosity and considerably lowered adsorption of water vapor below 0.5 relative pressure.

Studebaker and Nabors (*271*) found that when carbon blacks and sulfur were heated together at 150°C, hydrogen sulfide was evolved and that the resulting product contained sulfur which could not be removed by extraction with carbon disulfide. The amount of sulfur added to the carbon black was proportional to the product of the hydrogen content and the surface area of the sample. The presence of oxygen had an adverse effect and therefore fixation of sulfur was slightly lower in channel blacks than in furnace blacks for comparable values of the products of hydrogen content and surface area.

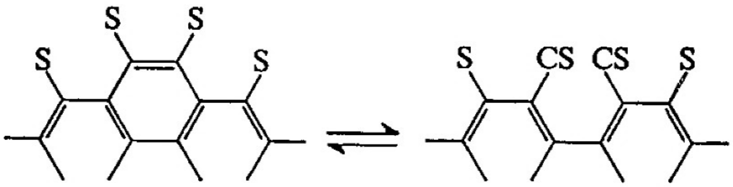
Dogadki, Skorodumova, and Kovaleva (*272,273*) showed that carbon blacks take up sulfur from a saturated solution in toluene on heating to 145°C in the presence of an accelerator. The amount was less if oxygen was present but more if hydrogen was present in the black. The combined sulfur did not affect moisture adsorption below 0.5 relative pressure, and could not be exchanged for radioactive sulfur. There were indications that sulfur was fixed as C—S—C or C—S—S—C groups.

Hofmann and Ohlerich (*156*) on heating activated sugar charcoal and sulfur at 600°C found that nearly 20% of the sulfur was fixed and that this was equivalent to the amount of oxygen fixed when the same charcoal was heated in oxygen at 400°C. These results indicated that the binding of sulfur by carbon is similar to that of oxygen. The sulfurized samples could catalyze the decomposition of sodium azide by iodine (*151*)

$$2NaN_3 + I_2 \rightarrow 2NaI + 3N_2$$

from which they concluded that the combined sulfur was present as sulfide groups.

Sykes and White (*274*) studied the interaction of coconut charcoal with sulfur, and also with carbon disulfide, at low pressures, in the temperature range of 627°–927°K. The adsorption of sulfur was found to be accompanied by the evolution of carbon disulfide. But when the same sample was treated with carbon disulfide, a pressure of sulfur was developed, indicating that now the reverse reaction was taking place. They concluded that sulfur and carbon disulfide were being adsorbed at the same set of sites, giving rise to different interconvertible structures containing sulfur. The following structures were suggested:



Puri, Balwar, and Hazra (*275*) heated charcoals outgassed at different temperatures with five times their weights of sulfur at 600°C. Besides evolution of hydrogen sulfide, there was appreciable fixation of sulfur, varying from 10–40% by weight, depending upon the hydrogen and oxygen contents of the sugar and coconut charcoals. The fixation was shown to take place partly in substitution of quinonic and phenolic groups and partly by addition at the unsaturated sites. In the case of charcoal outgassed at 1000° or 1200°C, almost the entire amount of sulfur was fixed by addition at the unsaturated sites and was equivalent to the amount of such sites as determined by bromine value (*182*). The formation of hydrogen sulfide in the reaction of carbon with sulfur introduced certain complications and it was not possible to separate the effect of sulfur from that of hydrogen sulfide, as had been pointed out by Studebaker (*271*).

Blayden and Patrick (*276*) studied the reaction between representative polymer carbons with sulfur vapor or hydrogen sulfide. They observed simultaneous loss of unpaired spin centers with fixation of sulfur and therefore concluded that the sulfurized products contained carbon–sulfur complexes. Apart from spin-pairing of sulfur with spin centers there was also substitution of combined hydrogen by sulfur at the easily accessible carbon surface. The concentrating of unpaired spin centers with the hydrogen content of the carbon therefore played an important role in the reaction. According to these workers, the carbon–sulfur binding in these complexes, which is akin to that in thioethers and disulfides, may lead to the formation of peripheral heterocyclic structures on the layer lattices in the carbon surface, or to sulfur bridges between the adjacent layer. Evidence for sulfides was suggested by the reaction of sodium azides with iodine. Interlamellar bonding of sulfur atoms was excluded on stereochemical grounds and also because no such compound is found even in macrocrystalline graphite where conditions for such formations are more favorable.

Owen, Sykes, Thomas, and White (*277*) studied the reaction of hydrogen sulfide with various types of carbons by a flow method between 1000° and 1600°K. There was appreciable formation of carbon disulfide but it was not clear whether this substance was produced by direct interaction of hydrogen sulfide and carbon or through the formation of some intermediate surface compounds. Polansky, Knapp, and Kinney (*278*) investigated the reaction of hydrogen sulfide with coal at 900° and at 1000°C, using two different concentrations (4.2 and 8.8 mole per cent) of hydrogen sulfide in nitrogen. An appreciable fixation of sulfur was reported in every case. The condition of the coke and the temperature and partial pressure of hydrogen sulfide played an important role in the amount of sulfur fixed by coke.

Studebaker and Nabors (*271*) studied the reaction of hydrogen sulfide with a few carbon blacks at 150° and at 600°C. There were two reactions at 150°C; one rapid and one slow. The rapid reaction, completed in 15–30 min, was found to be directly proportional to the oxygen content as 1,4-quinone groups, as estimated by catalytic hydrogenation in the presence of Adams catalyst. The correlation obtained between the two quantities indicated that there was addition of one sulfur atom for each quinone-type oxygen atom. The slow reaction was considered to involve substitution of hydrogen and this view was supported by the fact that the amount of sulfur fixed was proportional to the hydrogen content times the surface area of the carbon black. The slow reaction was retarded by oxygen atoms. Baraniecki, Riley, and Streeter (*279*) also studied reactions of carbonaceous materials with hydrogen sulfide.

Puri, Jain, and Hazra (*280*) studied the reaction by passing the gas at 2 liters/hr over charcoal placed in a rotating silica tube which could be heated electrically to any desired temperature up to 800°C. The gas, although highly stable, was found to decompose even at 100°C when passed over charcoal, resulting in the formation of a carbon–sulfur solid complex. The maximum formation of the complex was observed when the gas was passed over charcoal heated at 600°C for six hours. The amounts of combined sulfur decreased with a decrease in the hydrogen and oxygen contents of the charcoal on outgassing it at different temperatures before the treatment. The fixation of sulfur was found to take place by addition at unsaturated sites, as well as by substitution of hydrogen or oxygen or hydroxyl groups initially present on the charcoals.

Reactions of aqueous hydrogen sulfide with carbon blacks were examined by Karpinski and Swinarski (*281–283*) and with charcoals by Puri, Kaistha, and Hazra (*284*). The maximum value with charcoal was obtained by using $0.1N$ solution of the gas for about 100 hr. The amount of sulfur fixed varied between 5 and 6% by weight.

Carbon disulfide has also been used as a sulfurizing agent. Studebaker and Nabors (*271*) studied the reaction with carbon blacks at 150°C and observed a notable increase in the sulfur content of the blacks. Imada and Ono (*285*) studied the following reaction

$$CS_2 \rightleftharpoons C + S_2$$

by passing carbon disulfide or sulfur vapor in a stream of nitrogen over active carbon at 800°–1100°C. The reaction proceeded mainly from left to right up to 1000°C and thereafter reversed its direction. From the heat of the reaction, they concluded that sulfur was chemisorbed on the carbon surface as a first step of the reaction.

Puri, Jain, and Hazra (*280*) found the fixation of sulfur on treatment with carbon disulfide vapor at the optimum temperature of 600°C to be much more than that on treatment with hydrogen sulfide at the same temperature, particularly in those carbons which contained 2% or more of hydrogen. The hydrogen content was found to play an important role. This was attributed to the reaction of hydrogen evolved from the charcoal during the treatment with carbon disulfide, resulting in the production of hydrogen sulfide and sulfur which also act as sulfurizing agents:

$$CS_2 + H_2 \rightarrow H_2S + S + C$$

Sulfur dioxide is known to be adsorbed considerably on activated carbons, values as high as 22% at 40°C, 25% at 30°C, and 28% at 20°C have been reported. Desorption at 200°C gave relatively purer sulfur dioxide (*286*). Rassow and Hofmann (*287*) studied the reaction of sulfur dioxide and carbon at different temperatures. At 700° species like COS, CO_2, CO, S, and traces of carbon disulfide, were formed. The maximum formation of carbon disulfide was observed between 850° and 900°C. At higher temperatures, the main products of the reaction were carbon monoxide and monoatomic sulfur formed by the dissociation of COS, as confirmed by Siller (*288*). The monoatomic sulfur was considered to be responsible for the production of carbon disulfide.

Fisher and Pranscke (*289*) showed that the product obtained by reacting carbon with sulfur dioxide contained up to 35% of sulfur by weight. Stacy, Vastola, and Walker (*289a*) studied the reaction in a flow system by passing sulfur dioxide (0.5 vol%) mixed with helium through a packed bed of a medium activated coconut shell charcoal. There was very little chemisorption, covering hardly 1% of the surface in the temperature range 50°–350°C. At 650°C the reaction became rapid forming gaseous oxides of carbon and depositing elemental sulfur. Puri, Balwar, and Hazra (*275*) on treating charcoals with sulfur dioxide at 600°C obtained products that contained up to 27% of sulfur. On evacuating at high temperatures, a part of the combined sulfur came off as sulfur dioxide. There was also evolution of a small amount of carbon dioxide. These facts indicated possibilities for chemisorption of sulfur dioxide as such as well as oxygen during the interaction with sulfur dioxide.

The carbon–sulfur complex was highly stable. It was not possible to recover any of the combined sulfur even by boiling it with 2.5*N* NaOH under reflux for 12 hr (*290*). If the product was outgassed at increasing temperatures, the sulfur started coming off as hydrogen sulfide and carbon disulfide at 500°C, the amount increasing with rise in temperature (*290*). An appreciable amount of the sulfur was retained, however, even after outgassing the product at 1200°C. The entire amount of sulfur could be recovered as hydrogen sulfide only on treatment with hydrogen at 900°C.

The exact identification of the sulfur-containing groups formed on treatment of carbons with different sulfurizing agents has not been possible so far. The work in our laboratory (*275*,*280*) has shown that in all treatments sulfur is fixed partly at the unsaturated sites, which probably correspond to the unpaired spin centers of Blayden and Patrick (*276*), and partly by interaction with quinonic and phenolic hydroxyl groups.

An attempt was also made in the author's laboratory (*291*) to explore the nature of the sulfur groups formed as a result of interacting charcoals with sulfur, hydrogen sulfide, sulfur dioxide and carbon disulfide at the optimum temperature of 600°C. The products were treated with various oxidizing solutions (aqueous chlorine, acidified potassium chlorate, and concentrated nitric acid) and the amount of sulfur recovered in each case was estimated.

It was found (see Table XIII) that except when sulfur dioxide was used for the formation of the complexes, only part of the combined sulfur (depending upon the nature of the reaction used in formation of the complex) could be recovered even from a most drastic treatment with

TABLE XIII

Recovery of Sulfur from Different Charcoals on Treatment with Different Oxidizing Agents

Description of sample	Total sulfur fixed, mEq/g	Amount of sulfur recovered on treatment with, mEq/g		
		Aqueous chlorine	Acidified $KClO_3$	Hot nitric acid
400°C—Outgassed sugar charcoal				
Treated with CS_2	9.30	0.16	0.17	0.48
Treated with H_2S	7.00	2.85	—	3.18
Treated with S	11.10	3.87	4.23	4.12
Treated with SO_2	16.60	10.27	13.47	15.07
400°C—Outgassed coconut charcoal				
Treated with CS_2	11.00	0.06	Nil	0.82
Treated with H_2S	7.05	2.33	1.00	3.25
Treated with S	10.50	4.05	2.09	4.86
Treated with SO_2	11.90	10.70	10.40	10.70
1000°C—Outgassed sugar charcoal				
Treated with CS_2	5.00	Nil	Nil	0.36
Treated with H_2S	5.50	0.90	0.58	1.55
Treated with S	5.61	0.70	0.80	1.68
Treated with SO_2	5.40	4.90	5.00	5.31
1000°C—Outgassed coconut charcoal				
Treated with CS_2	5.50	0.34	Nil	0.32
Treated with H_2S	4.30	0.81	0.70	0.65
Treated with S	4.80	1.20	1.25	1.40
Treated with SO_2	4.20	3.75	3.90	4.10

nitric acid at 110°C. This indicated that sulfur was fixed at more than one site and that it gave rise to more than one kind of sulfur group.

Almost the entire amount of sulfur fixed on treatment with sulfur dioxide was oxidized by hot nitric acid, and, in some cases, even by chlorine water. It appears that the more readily oxidizable sulfoxide groups are formed (*287*), in addition to equally easily oxidizable sulfide and polysulfide groups attached to the side chains. The formation of sulfoxide groups is supported by the fact that an appreciable amount of oxygen was evolved in the form of sulfur dioxide and carbon dioxide when the products were outgassed, as mentioned previously.

In charcoals treated with hydrogen sulfide, an amount of sulfur closely equivalent to surface unsaturation (3.9 mEq/g) for both sugar charcoal and coconut charcoal, was fixed so firmly that it could not be released even when treated with an excess of hot concentrated nitric acid. The rest of the combined sulfur was released almost fully on oxidation with nitric acid and substantially even with chlorine water. It appears that quinonic and phenolic hydroxyl groups, which are present in appreciable amounts particularly in charcoals outgassed at 400°C, are involved in the interaction with hydrogen sulfide, and give rise to thioquinone and thiophenol groups. Studebaker has also indicated such possibilities (*271*). It is significant to note that the amount of sulfur released as sulfuric acid is much more in charcoals outgassed at 400°C than in those outgassed at 1000°C. This is because the former contained much more oxygen than the latter. The amount of sulfur that is not released is seen to be about the same, however, because surface unsaturation was not very different in the samples of the two categories. It appears probable that sulfur fixed on treatment with hydrogen sulfide gives rise to the reactive thioquinone or/and thiophenol groups by interacting with quinones and phenol groups already present on the surface, as well as to the nonreactive structures by the fixation of sulfur at the unsaturated sites.

The treatment with sulfur involves a combined action of sulfur vapor and hydrogen sulfide, as already mentioned. Therefore, in addition to the formation of reactive and nonreactive groups by the reaction of hydrogen sulfide as just discussed, some additional sulfur is likely to be fixed at certain active sites where formation of C═S groups is possible, analogous to the formation of quinone groups from similar treatment with oxygen. The results indicate that only a part of this sulfur can be recovered on oxidation.

The amount of sulfur recovered from charcoals treated with carbon disulfide constituted only 6–7% of the total sulfur fixed, even when the oxidizing treatment was very drastic, such as heating with concentrated nitric acid at 110°C. This reaction with carbon disulfide evidently gives rise to highly stable surface compounds because carbon is also deposited through the action of the hydrogen evolved from the charcoal during the process. It is not unlikely that new peripheral heterocyclic structures are also condensed on the layer lattices in the carbon surface.

The sulfurized products were found (*291a*) to catalyze the sodium azide–iodine reaction, evolving nitrogen, to a considerable extent. Further, it was found that sulfur groups formed by a substitution process, involving interaction with quinonic and phenolic groups, were catalytically much more active than those formed by fixation of sulfur at the unsaturated sites. This indicated the probability of the presence of sulfide and hydrosulfide groups in the former case and heterocyclic ring structures in the latter case.

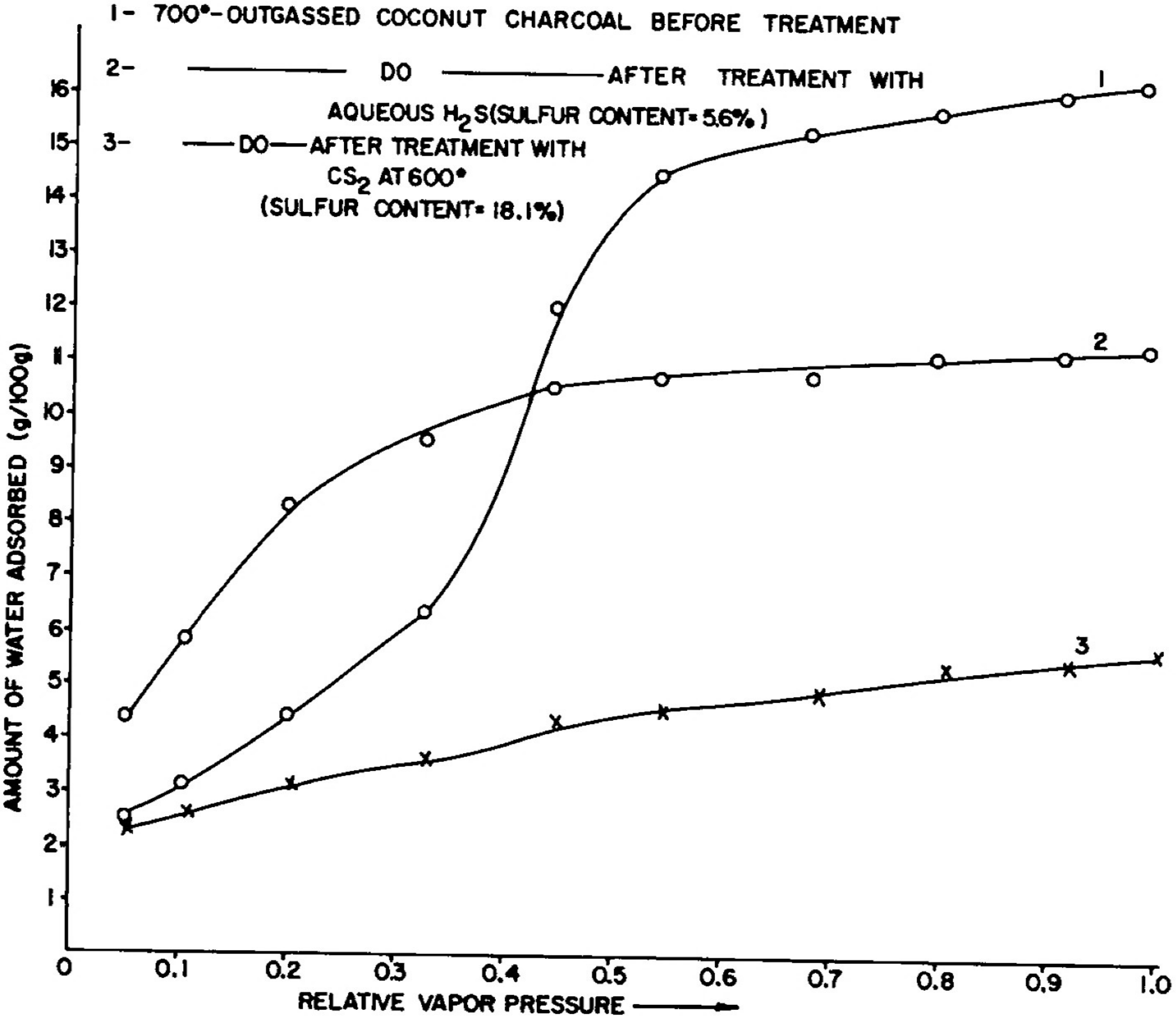


Fig. 17. Water isotherms of coconut charcoal outgassed at 700°C before and after fixation of sulfur.

The effect of fixation of sulfur on sorption of water vapor by charcoal, free from the side effects of heat treatments, was studied by determining water adsorption isotherms (35°C) on some of the charcoals before and after treatment with aqueous hydrogen sulfide at room temperature (*292*). The results obtained in one such study are plotted in Fig. 17. It can be seen that there is an appreciable increase in the sorption of water at relative vapor pressures below 0.4 and a considerable decrease thereafter. The results indicate narrowing down of capillary pores as well as decrease in porosity as a result of fixation of sulfur.

The water adsorption isotherm obtained on the same charcoal after fixation of about 18% of sulfur, as a result of treatment with carbon disulfide at 600°, is also shown in Fig. 17. There is now a considerable fall in the values at all relative humidities. The sulfur complexes appear to be particularly suitable for minimizing adsorption of water vapor on charcoals.

VII. CONCLUSIONS

Carbon is regarded as a unique element for several good reasons. One such reason is its remarkable property of chemisorbing other elements, notably oxygen, hydrogen, nitrogen, halogens, and sulfur, which gives rise to stable solid compounds, usually called surface complexes. An attempt has been made in the present chapter to give a critical review, together with some pertinent details, of the research work that has been conducted in recent years in this field with particular reference to formation, stability, structure, and properties of the various surface complexes.

As can be seen there are several aspects that require further investigation even with regard to the carbon–oxygen systems which have received the most attention so far.

For example, an appreciable amount of the combined oxygen has not yet been chemically identified, the nature of the acidic surface oxides has not been properly understood, the methods for estimating the groups that have been identified so far have not yet been standardized. The work reported on surface complexes of carbon–hydrogen, carbon–nitrogen, carbon–halogens, and carbon–sulfur is comparatively small. The mechanism of fixation, the location of the sites, the nature of the bond, and the structure of the functional groups, if any, all need elucidation.

The relatively easy manner in which the various complexes can be obtained, particularly on the surface of microcrystalline carbons, and the profound influence which they exercise in altering surface properties, such as acidity, cation-exchange capacity, wettability, porosity, selectivity in adsorption, and so on, are likely to be useful in improving several conventional applications of carbons as well as in finding some newer application of these materials. This is a field where physical chemists, organic chemists, fuel technologists, spectroscopists, solid-state physicists, and—last though by no means the least—industrial research workers, have plenty of scope for further investigations.

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