Chemistry and Physics of Carbon

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CHEMISTRY AND PHYSICS
OF CARBON

Volume 6

CHEMISTRY AND PHYSICS OF CARBON

A SERIES OF ADVANCES

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Volume 6

1970
MARCEL DEKKER, INC. New York

MARCEL DEKKER, INC.
95 Madison Avenue, New York, New York 10016

LIBRARY OF CONGRESS CATALOG CARD NUMBER 65-27434

PRINTED IN THE UNITED STATES OF AMERICA

PREFACE TO VOLUME 6

Following the objectives of this monograph series as outlined in the first volume, Volume 6 of the *Chemistry and Physics of Carbon* series is concerned with comprehensive reviews of past achievements in important areas of carbon.

We are most happy to have a contribution from A. V. Kiselev and his school from Russia in this volume. The school is noted for their studies in the area of physical adsorption on solids. In chapter one, Avgul and Kiselev achieve and present a detailed interpretation of the fundamental adsorption parameters which describe the interaction between adsorbate molecules and homogeneous carbon surfaces and interaction of adsorbate molecules with each other. Of particular value is the vast amount of data and correlations which they present for hydrocarbon adsorption. These results have particular relevance today because of our concern about environmental control through the use of porous carbons to remove organics from the atmosphere and our streams.

It is always exciting in the field of materials science when it is possible to quantitatively relate the structure of solids to some property. J. Méring and his school in France have long made significant contributions to our understanding of the structure of carbons through their crystallographic studies and changes which the structure undergoes on graphitization. They have particularly been concerned about the effect of heat treatment on altering the density of defects in carbons, such as stacking faults and interstitial species. In this chapter, Maire and Méring show relationships between carbon structure and the propensity of the structure to take up bromine, as the structure is altered upon graphitization. It is one of the first cases, of which the editor has knowledge, where adsorption is clearly related to the Fermi level in the solid. In turn the Fermi level is affected by the level of defects in the solid, as they show.

It is increasingly recognized that the behavior of solids in many applications is significantly affected by the nature and state of the surface. This is particularly true of many porous carbons where the surface to volume ratio is relatively high. In Chapter 3, Puri presents a comprehensive picture of the formation of the important surface complexes on carbon surfaces, that is complexes containing oxygen, hydrogen, nitrogen, halogens, and sulfur. In most cases these complexes are covalently bonded to the surface. Puri also discussed the effect which the presence of the complexes on carbon surfaces have on the behavior of the carbons for different applications.

In Volume 4 of this series Tsuzuku and Saito had a chapter on "Internal Friction Studies on Graphite." In this review they considered briefly the effect of irradiation of graphite on internal friction, showing that it is particularly sensitive to the formation of point defects. Now Taylor and Kline in Chapter 4 of this volume extend considerably our understanding of the mechanism of radiation damage in graphite by following changes in dynamic mechanical properties. It turns out that internal friction is probably the most sensitive tool which we have to follow irradiation damage in graphite, it being much more sensitive than following changes in electronic or thermal transport properties, for example.

P. L. W., Jr.

University Park, Pennsylvania
December, 1969

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CHEMISTRY AND PHYSICS
OF CARBON

Volume 6

SURFACE COMPLEXES ON CARBONS

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I. INTRODUCTION

When two phases are brought into contact with each other, it frequently happens that one phase, or some constituent of it, gets concentrated more at the interface than in the bulk. This phenomenon of higher concentration at the interface is called adsorption. Thermodynamically, adsorption is accompanied by a decrease in free energy as well as a decrease in entropy of the system. If accumulation at the interface arises from dispersion forces (van der Waals or London forces), the phenomenon is known as physical adsorption or "physisorption"; and if it occurs as a consequence of exchange or sharing of electrons, giving rise to ionic or covalent bonds, the phenomenon is known as "chemisorption." Chemisorption proceeds, generally, more rapidly with rise in temperature, and, therefore, like most chemical reactions, involves an activation energy. It is therefore, also termed as activated adsorption. The enthalpy of adsorption is often used to differentiate between physisorption, in which the value is usually less than 8 to 10 kcal/mole, and chemisorption, in which the value is much higher, varying usually between 20 and 100 kcal/mole.

Because in chemisorption, adsorbate molecules are linked to the surface by valency bonds, a chemisorbed layer is only one molecule thick. In physisorption, on the other hand, the adsorbate gas may form monomolecular or multimolecular layers. The latter possibility arises at pressures approaching the saturation pressure of the adsorbate.

One of the very early examples of chemisorption was furnished by Langmuir during his work on the interaction of oxygen with carbon (*1*) and tungsten (*2*) filaments. The gas was held so firmly that it came off when heated as oxides of carbon and tungsten, respectively. Some other examples of chemisorption reported in the early literature are those of oxygen on silver (*3*) and gold (*4*), carbon monoxide and oxygen on manganese dioxide and cupric oxide (*5*), carbon monoxide on tungsten (*2*), hydrogen and carbon monoxide on zinc oxide-chromic oxide mixtures (*6*), and water vapor on graphite (*7*). The study of chemisorption at the solid/gas interface has assumed considerable importance in recent years as it helps in understanding mechanisms of surface reactions and finds applications in heterogeneous catalysis.

A very large number of studies of chemisorption of gases and vapors have been made on carbons of diverse forms, ranging from well defined crystalline materials, such as diamond and graphite, to amorphous or microcrystalline materials, such as chars, activated carbons, carbon blacks, and cokes. In carbons, the fraction which exists in the form of disordered, single, unstacked graphite-like layers is more susceptible, while the fraction which shows some degree of well-ordered parallel stacking, is less susceptible to chemisorption of gases and vapors. The disordered fraction is higher in microcrystalline carbons than in crystalline carbons. At the same time there are many exposed defects, dislocations and discontinuities in the layer planes of the microcrystalline carbons, apart from the edges of the carbon layers. Such sites, called the "active" sites, are associated with high concentrations of unpaired electron spin center and, therefore, are expected to play a significant role in chemisorption. Moreover, charcoals and activated carbons, being porous, and carbon blacks, being composed essentially of spherical particles of colloidal dimensions, have large internal and external surface areas for unit weight respectively.

It is for these reasons that microcrystalline carbons—although poorly defined materials, with composition and character that vary with the history of their formation—have been of great interest in the field of chemisorption. The surface carbon atoms located at the active sites, due to residual valencies, show a strong tendency to chemisorb other elements, like oxygen, hydrogen, nitrogen, chlorine, bromine, iodine, and sulfur and give rise to nonstoichiometric stable surface compounds, called surface complexes. Many of the surface reactions of charcoals and carbon blacks arise either because of their tendency to chemisorb other elements or because of the existence of a superficial layer of the chemically bonded elements.

Oxygen is chemisorbed more readily than many other elements are, and carbon-oxygen complexes are by far the most important in influencing surface reactions, surface behavior, wettability, and electrical and catalytic properties of carbons. These complexes, therefore, have been discussed first in the present section.

II. CARBON-OXYGEN SURFACE COMPLEXES

A. Historical

Smith (*8*), in 1863, was probably the first worker to suggest that when oxygen is adsorbed on a carbon surface it undergoes a chemical change. He found that adsorption of oxygen on charcoal did not cease even after a month; and that while nitrogen and other gases adsorbed on charcoal could be easily removed as such, oxygen could be removed only on strong heating, and then as carbon dioxide. Baker (*9*), a few years later, showed that an outgassed charcoal could "fix" oxygen even at −13°C. Rhead and Wheeler (*10,11*) concluded that oxygen combines with a mass of carbon directly to form a physicochemical complex, C_xO_y, of variable composition, which decomposes over a wide range of temperature, giving a mixture of carbon monoxide and carbon dioxide. These observations were confirmed by Lowry and Hulett (*12*), who, while attempting to determine the content of the moisture and gas in charcoal, noticed that the gases evolved up to 900°C consisted almost entirely of carbon dioxide and carbon monoxide, the former predominating at lower temperatures and the latter at higher temperatures.

Further evidence for chemisorption or fixation of oxygen on carbons was furnished by the work of Langmuir (*1*), Lambert (*13*), Lepin (*14*) and others (*15,16*). Ward and Rideal (*17*) found that the heat of adsorption of oxygen on charcoal, even at 0°C, was of the order of 40 kcal/mole, suggesting the chemical nature of the interaction involved. Other workers (*18–21*) reported even higher values, varying from 60 to 84 kcal/mole.

It is now known that almost all types of carbons are covered with oxygen complexes unless special care is taken to eliminate them. These complexes are often the source of the property by which a carbon becomes useful or effective in certain respects.

B. Formation of Carbon–Oxygen Complexes

Several methods of forming carbon–oxygen surface complexes have been reported in recent years. These may be classified into two broad categories: methods involving reactions with oxidizing gases; and methods involving reactions with oxidizing solutions.

1. Methods involving reactions with oxidizing gases

a. Reactions with oxygen

The procedure generally employed (*22,23*) consists in passing oxygen at the rate of 2 to 3 liter/hr over 5–10 g carbon contained in a rotating borosilicate tube placed in a tube furnace, which can be heated electrically to a desired temperature. It has been found that the optimum temperature for the maximum chemisorption of oxygen lies close to 400°C and that the capacity of charcoal to chemisorb oxygen depends upon its surface area and content of hydrogen. For example, the oxygen content of sugar charcoal, outgassed at 1200°C with surface area of 405 m^2/g, could be raised to about 14%, while that of coconut charcoal, outgassed at the same temperature but with surface area of 349 m^2/g, could be raised to only a little more than 8% (*22*). The hydrogen content of these samples was about 1.02 and 0.61%, respectively.

The complex that can evolve carbon dioxide (CO_2–complex) is formed to the maximum extent at 400°C. It starts decomposing if treatment is given at higher temperatures. The complex that can evolve carbon monoxide (CO complex), however, also formed to the maximum extent around 400°C, remains more or less unchanged even if the treatment is given at higher temperatures up to 600°C. There is also a certain optimum pressure of oxygen, lying between 0.7 and 0.8 atm. (*24*), for maximum fixation of oxygen at 400°C. As the pressure is increased towards one atmosphere, both the complexes start decomposing to a small extent. Watt and Franklin (*25*) studied chemisorption of oxygen on charcoals of varying hydrogen contents. The amount of oxygen chemisorbed varied from 3 to 25%. By using ozonized oxygen they could raise the oxygen content to 40%. Earp and Hill (*26*) extended these treatments to industrial carbons, varying the temperature up to 700°C, while Snow et al. (*27*) experimented with carbon blacks, restricting the temperature up to 400°C. From X-ray and analytical data of the products and surface area measurements of the carbon blacks, Snow et al. concluded that chemisorbed oxygen was fixed not only on the surface of the carbon particles but also up to 10–20 Å into the interior of the surface. There was an appreciable increase in surface area during oxidation and again during elimination of the resulting complex. The activation energy of the process was found to be 25 to 30 kcal/g atom of carbon oxidized.

Lobenstein and Deitz (*28*) studied chemisorption of oxygen on a few carbon adsorbents, including a sample each of bone charcoal, coconut charcoal, and channel black, at 200°C. They differentiated between oxygen used in chemisorption and oxygen used in combustion. Deitz and McFarlane (*29*) examined adsorption of oxygen on evaporated films of high surface area at temperatures between 100 and 300°C and reported that chemisorption was rapid in the beginning and slowed down afterwards. The slowing was believed to be a reaction between molecular oxygen and surface carbon atoms. Allardice (*30*) experimented with charcoals at temperatures between 25° and 300°C, using oxygen in the pressure range of 160–760 mm Hg, and observed a similar two-step adsorption. The rapid adsorption was found to be reversible, while the slow adsorption was found to be irreversible and to follow the Elovich rate equation, i.e., the plots of amounts adsorbed versus log of time were linear.

Kiselev et al. (*31*) oxidized channel blacks in air at 450°C and observed increases in the capacity for adsorbing water, methanol, hexane, and benzene vapor. This was attributed to development of micropores. Donnet and Papirer (*32,33*) studied oxidation of Philblack by ozone and found the rate to be maximum at 100°C. From the examination of electron- and X-ray diffraction, it was concluded that oxidation occurred mostly on the amorphous part of the carbon and that it caused granulation and development of oxygen-containing functional groups. Medalia et al. (*34*), using low temperature adsorption and electron microscopic techniques, found that the oxidation of carbon black with oxygen in the 300–400°C temperature range depended on temperature and resulted in alteration of pore-size distribution and formation of surface oxides.

A few studies on the kinetics of chemisorption of oxygen on carbons at different temperatures and under different pressures have also been made. Landle (*35*), using sugar-charcoal in the temperature range of 0–350°C, found the data to follow the empirical formula

$$q = k_1 - k_2 \exp(-k_2 t)$$

The $q - t$ curves showed a rapid adsorption during the first 10–20 min, and a slow uptake subsequently. The data were too few to permit proper interpretation of the Elovich plots. Carpenter and Giddings (*36*) and Carpenter and Sergent (*37*), while studying oxidation of coal at 65°, 85°, and 105°C, found that the quantity of oxygen sorbed during the first 5 min was in accordance with the Elovich equation; but afterwards it exceeded the value predicted by the equation.

Until 1959, data regarding kinetics of chemisorption of oxygen on carbons in general and on pure carbons in particular were regarded as scanty (*38,38a*). In recent years, however, Walker and co-workers have made thorough studies on graphites of high grade purity. The work has been nicely summed up elsewhere in the present series (*39*). Working with highly crystalline natural graphite in the temperature range of 335–450°C and an oxygen pressure of 760 mm Hg and using thermoelectric power measurements (*40,41*), Walker et al. found the rate constant of the reaction to be independent of surface coverage, unlike the situation under which the Elovich equation is applicable. By using the ^{18}O isotope in oxygen mixtures, in a reactor at low pressure and low temperature, they showed that a surface oxide is produced during the reaction and that carbon monoxide and carbon dioxide are the primary products of the reaction. Further, both oxygen atoms of the carbon dioxide do not come always from the same molecule of oxygen (*42*).

Walker and co-workers (*43–46*) also studied chemisorption of oxygen in the temperature range 300–625°C at low pressures up to 0.5 mm Hg on Graphon, a highly graphitized carbon black which was previously oxidized to different burn-offs in oxygen at 625°C, to introduce significant amounts of active surface area. The samples were cleaned at 975°C in vacuum of 10^{-5} mm Hg before each experiment. They used mass spectrometric techniques to follow the rate of chemisorption. A sharp increase in the saturation amount of oxygen adsorbed at temperatures of about 400°C was observed. This suggested the presence of two types of active sites. They derived an equation (*44*) according to which the rate of chemisorption on the more active sites (Type I) at a given time was calculated from the concentration of oxygen in the gas phase, the total number of Type I sites and the square of the fraction of such sites that are not covered at that time. The oxygen fixed at these sites was supposed (*45*) to give rise to lactones, which are considered to evolve carbon dioxide on thermal decomposition, while that fixed at Type II sites was supposed to give rise to carbonyl groups, which are considered to come off as carbon monoxide. The repeated cycles of sorption and desorption produced new active sites which could not be produced on activation in the temperature range of 500–625°C for comparable burn-offs. The amount of the surface complex formed at 300°C in 24 hr with an oxygen pressure of 0.5 mm Hg was found to be maximum (*43*). The gases evolved on outgassing (carbon monoxide and carbon dioxide) were converted into oxygen atoms and assuming that the complex consists of one oxygen atom for one active (edge) carbon atom (occupying an area of 8.3 $Å^2$), the total active surface area in the Graphon sample was found to be 2–3% of the BET area. This decreased further with increase in the temperature of reaction beyond 350°C, and this led to the suggestion that only the carbon atoms located at the edges of the basal planes were active in chemisorbing oxygen (*47*).

At 625°C, however, the amount of the surface covered by the chemisorbed oxygen (*48*) was about the same as that covered by the physical adsorption of nitrogen in the low relative pressure range. It was suggested, therefore, that chemisorption of oxygen at 625°C occurs not only at the edge atoms but also at lattice intersections and defects. Hennig (*49*), from microscopic examination of single graphite crystals, concluded that at temperatures below 800°C the oxidation rate of the edge carbon atoms was about 20 times as high as that of the carbon atoms at the cleavage surfaces. The edge carbon atoms were almost completely covered with oxygen complexes even at such a low pressure as 0.1 mm Hg at temperatures below 700°C.

Adsorption of oxygen on diamond was investigated by Barrer (*50*), and was found to involve mainly physical adsorption at −78°C and predominantly chemisorption between 0° and 198°C. Carbon dioxide was produced between 244° and 370°C, but the amount of the gas produced was much smaller than the amount of oxygen taken up, showing that a part of the oxygen was still being chemisorbed. The surface complex decomposed into carbon monoxide and carbon dioxide at higher temperatures. Boehm (*51*) claimed formation of surface oxides on diamond powder of 17 m^2/g surface area by treating it in oxygen at 400°C, or with sodium hypochlorite and ammonium persulfate solutions at room temperature. The diamond powder became hydrophilic as a result of surface oxidation but became hydrophobic again on outgassing at 800°–900°C.

Several attempts have been made to understand the phenomenon of combustion but no comprehensive theory that accounts satisfactorily for all the facts has been put forward so far. There is considerable evidence, however, (*38*,*52–55*) that the primary step in combustion is dissociative adsorption of oxygen to form oxygen complexes. Below 500°C, the rate of formation of these complexes exceeds their rate of decomposition, but at higher temperatures the complexes become less stable and the rate of their decomposition into carbon dioxide and carbon monoxide exceeds the rate of their formation. The formation of carbon dioxide and carbon monoxide requires an appreciable concentration of oxygen complexes. It has also been shown, by using ^{18}O, that the breakdown of the oxygen complexes contributes somewhat to the total of carbon monoxide and carbon dioxide produced during the combustion of carbon (*44*).

b. Reactions with oxides of nitrogen

A number of reactions between carbons and the oxides of nitrogen resulting in the chemisorption of oxygen have been reported. Shah (*56,57*) found formation of an adsorption complex of oxygen at the charcoal surface an important step during combustion of charcoal in atmospheres of nitrous oxide and nitric oxide. Strickland-Constable (*58*), and later Madley and Strickland-Constable (*59*), showed that an outgassed charcoal, when treated with nitrous oxide at 300°C, picked up an appreciable amount of oxygen, giving rise to stable surface complexes. These findings were confirmed by Smith and co-workers (*60*). Using Graphon and sugar charcoal they found that the interaction with nitrous oxide in the temperature range of 400–650°C, involved first a rapid oxidation of the active centers, giving rise to carbon–oxygen surface complexes and free nitrogen. This oxidation was followed by a slow reaction in which the complexes were oxidized to gaseous carbon dioxide and more free nitrogen was produced. The following reaction mechanism was suggested:

$$N_2O + C \xrightarrow{\text{fast}} N_2 + \underset{\text{surface complex}}{(CO)}$$

$$N_2O + (CO) \xrightarrow{\text{slow}} N_2 + CO_2$$

$$(CO) \longrightarrow CO$$

Later, Smith et al. extended this work by using nitric oxide (*61*) in place of nitrous oxide. This reaction was conducted in the low temperature range, between −78° and 0°C, as well as in the high temperature range, going up to 600°C. A rapid fixation of oxygen with production of free nitrogen was observed even in the low temperature range and this continued with increasing intensity up to 200°C. No gaseous carbon dioxide was evolved, however. The reaction ceased after the surface became saturated with oxygen. At higher temperatures, particularly between 450 and 600°C, the reaction was found to be of first order and to proceed continuously, yielding nitrogen, carbon monoxide, and carbon dioxide, besides surface oxygen complexes. The authors postulated that a molecule of nitric oxide reacts with another molecule adsorbed at the site of the oxygen complex on the surface to give nitrogen and carbon dioxide, and an oxygen complex on the adjacent carbon atom. The new oxygen complex served as a site for further adsorption of nitric oxide, and thus the reaction was continued. The preceding mechanism was represented by the following scheme:

$$2NO + 2C' \rightarrow N_2 + 2(C'O)$$

$$NO + (C'O) \rightleftharpoons (OC'\text{------}ON)$$

$$NO + (OC'\text{------}ON) + C'' \rightarrow C'O_2 + N_2 + (C''O)$$

$$NO + (OC'\text{------}ON) + C''' \rightarrow C'O_2 + N_2 + C'''O$$

The entities enclosed in the parentheses represent species chemisorbed on the carbon surface.

The reaction of outgassed sugar and coconut charcoals with nitrogen peroxide was studied by Puri, Singh, Kumar, and Sharma (*62*) at temperatures varying from 100° to 600°C. There was appreciable combustion of charcoal as well as fixation of oxygen, the optimum temperature for which was found to be about 400°C, as had been reported earlier (*22*) in the reaction with oxygen. The maximum amount of oxygen fixed was about 14% in sugar charcoal and about 8% in coconut charcoal. About the same values had been observed earlier from treatment with oxygen under similar conditions (*22*). These workers also studied the reaction at room temperature, using a chloroform solution of the gas. Nearly 5–10% of the gas was decomposed. Almost the entire amount of the oxygen rendered available was chemisorbed and was recovered as carbon dioxide on evacuation at high temperature. The oxygen content of the charcoals could be raised to the extent of 3.9 and 2.9%, respectively, using concentrated solutions of the gas.

c. *Reactions with water vapor*

A number of investigations have been reported on reactions of activated carbons and carbon blacks with water vapor at different temperatures, under static as well as dynamic conditions. The conclusions given, however, have not been always in harmony with one another. Smith, Pierce, and Joel (*63*) sealed their samples mixed with known amounts of water in small glass bulbs of 11–12 cc capacity, which were then placed in baths maintained at 25°, 100°, or 200°C for different periods of time up to 75 hr. The treatment resulted in the formation of a hydrogen complex as well as two oxygen complexes, one that decomposed easily as carbon dioxide and the other, which was more stable, decomposing as carbon monoxide when heated to about the softening point of Pyrex glass. It was also observed that carbon surfaces that already contained some chemisorbed oxygen reacted with water much more readily and continuously than did those without oxygen.

The work of Beeck (*64*) indicated that water is adsorbed by carbons with dissociation and that the product is a more effective dehydrogenating catalyst than the unreacted carbon is. Studebaker (*65*), on treating carbon blacks in a dynamic system in moist air and moist nitrogen at 65°C and subsequently drying them at 150°C in dry nitrogen, observed chemisorption of hydrogen but not oxygen. He explained the results by postulating that carbon blacks adsorb water molecules with dissociation and preferentially retain hydrogen.

Singh, Parkash, and Puri (*66*) studied the reaction between charcoal outgassed at 1200°C and steam at different temperatures from 200° to 1200°C. There was appreciable fixation of water as such, the amount being almost independent of the temperature of treatment. At the same time there was appreciable fixation of oxygen, the optimum temperature for which was again 400°C. The amount of oxygen fixed at this temperature after 4 hr of treatment was about 10%, nearly 60% of this was disposed of as carbon dioxide and the rest as carbon monoxide. The CO complex was formed only between 200° and 400°C and not at all at higher temperatures. This was explained as due to oxidation of this complex to gaseous carbon dioxide by water vapor at higher temperatures.

$$(\mathrm{CO}) + \mathrm{H_2O} \rightarrow \mathrm{CO_2} + \mathrm{H_2}$$

These observations are significant in showing that the more stable CO complex, which ordinarily can be desorbed completely only on heating in vacuum to about 1000°C, can be eliminated by heating in a current of steam for 6–8 hours even at 400°C. The steam–carbon reaction has been investigated also by some other workers (*67,68,69*).

d. Reactions with carbon dioxide

Reactions of carbon with carbon dioxide have been treated largely as gasification reactions and have been nicely reviewed by Walker, Rusinko, and Austin (*70*). It has been suggested (*71,72*) that carbon dioxide oxidizes carbons to carbon monoxide, forming oxygen complexes as intermediates. The various steps of the reaction are:

$$\mathrm{CO_2} + \mathrm{C} \xrightarrow{\text{fast}} \mathrm{CO} + (\mathrm{CO})$$

$$(\mathrm{CO}) \xrightarrow{\text{slow}} \mathrm{CO}$$

$$\mathrm{CO} + (\mathrm{CO}) \longrightarrow \mathrm{CO_2} + \mathrm{C}$$

Boulangier, Duval, and Letort (*73*) studied the kinetics of the reaction of carbon filaments with oxygen, carbon dioxide, and water vapor, at temperatures between 1300° and 2100°K and a pressure of 10^{-3} mm Hg. They showed that the reactions were of first order and that the maximum rate of gasification occurred around 1400°K for oxygen, at 1650°K for water vapor, and at 1550°K for carbon dioxide.

Blakeley (*74*) found that the rate of gasification of coconut charcoal and graphite by carbon dioxide was affected below 900°C by surface oxides, between 900–1000°C, by the type of the carbon as well as by the temperature and partial pressure of the gas, and above 1100° by diffusion, gas velocity, and partial pressure. The importance of the surface oxide, which is formed simultaneously with gaseous products, in determining the rate of gasification was also emphasized by Tonge (*75*). Walker and Nichols (*76*) determined reactivities of coke or graphitized carbons in carbon dioxide over the temperature range of 1000°–1200°C from the loss in weight.

Walker and Rusinko (*77*) examined gasification rates of carbon rods with carbon dioxide at temperatures varying from 900° to 1300°C, but found no correlation between average size of crystallite, porosity, or surface area, and the rate of gasification. Similarly, no significant correlation could be found between the microporous structure of the carbons and their rates of gasification (*78*). The equation for the kinetics of gasification was worked out (*79*) and a suitable mechanism of the reaction was proposed. Deitz, Carpenter, and Arnold (*80*) observed three increasing levels of interaction between carbon and carbon dioxide: (1) pure physical adsorption, (2) formation of an adsorption complex having a bicarbonate structure, and (3) formation of an adsorption complex with a carbonate structure.

A considerable amount of work has been done on the action of oxygen and carbon dioxide on the gasification of pure carbons at the French Atomic Energy Commission Laboratory by Lang and co-workers. This work has been nicely described in a chapter in Volume III of the present series (*81*). Ergun and Menster (*82*) have discussed at length the mechanisms of reaction of carbon with steam and carbon with carbon dioxide in a chapter in Volume I of the present series.

2. Methods involving reactions with oxidizing solutions

Reactions of carbons with various oxidants in aqueous solutions have been studied in detail by several investigators. The reactions generally involve surface oxidation as well as gasification of the carbon. The oxygen complex that is formed generally comes off mainly as carbon dioxide on thermal decomposition in vacuum. The nature and magnitude of the surface and the presence of chemisorbed oxygen, if any, are amongst the factors which influence the course of the reaction. Thus carbons having alkaline surface groups react more readily with acidified potassium permanganate than those having acidic surface groups (*83,84*). The reaction is slowed down considerably if the carbon is already associated with chemisorbed oxygen (*84*). It was inferred, therefore, that the surface complex consists of peracidic groups which do not reduce rather than peroxidic groups which reduce the permanganate. The kinetic studies indicated that two reactions were involved, one of which was fast and the other slow. Garten and Weiss (*85*) suggested that the fast reaction was due to the oxidation of chromenes (which according to them are present on the surface of many carbons) to lactones. If the chromenes had already been oxidized by previous chemisorption of oxygen, the activity of the carbon for the reaction would decrease, as had been reported (*84*).

Banerjee, Mazumdar, and Lahiri (*86*) showed that permanganate, whether acidic or alkaline, reacts vigorously with coal even at room temperature till the coal is degraded into water-soluble products. They could not detect the presence of carboxyl groups in the treated coal. Puri, Sharma, and Mahajan (*87*) found the reaction between charcoal and acidified permanganate to follow two distinct courses, one involving formation of manganese sulfate and the other, manganese dioxide.

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5(0) \ldots$$

$$2KMnO_4 + H_2SO_4 \rightarrow K_2SO_4 + 2MnO_2 + H_2O + 3(0) \ldots$$

The magnitude of the second reaction, at low concentrations of permanganate, was greater in the outgassed than in the original charcoals, and it increased with increase in concentration in both types of charcoals. At 0.7*N* concentration, almost the entire reaction was in accordance with the second reaction. The oxygen that was rendered available, in either case, was partly chemisorbed and partly consumed in gasifying charcoal to carbon dioxide. The fraction of the oxygen chemisorbed by the original charcoal was very small. It increased with increase in the temperature at which the charcoal had been outgassed before reaction with the permanganate.

The reaction of large graphite crystallites with potassium chlorate in a solution of concentrated sulfuric acid or with a mixture of sulfuric and nitric acids is known (*38*) to give "graphitic oxide," a product of indefinite composition. This substance cannot be obtained by treating graphite in oxygen, and certainly it is not a surface compound.

The reaction of charcoal or carbon black with nitric acid or a mixture of nitric and sulfuric acids has been investigated by several workers and the formation of such functional groups as carboxylic (*88*), phenolic (*89*) quinonic (*90*) and free radicals (*91*) has been suggested. The product has a larger surface area (*92*) and altered pore size distribution (*93*).

Donnet and Reiss (*94*) found the products obtained from carbon blacks to be highly hydrophilic and to disperse readily in polar organic solvents. The presence of hydroxyl and carboxyl groups was inferred from infrared absorption bands (*95*). Puri, Singh, and Mahajan (*92*) found that the products obtained on treating outgassed charcoals with hot concentrated nitric acid contained over 20% of oxygen, more than 90% of which came off as carbon dioxide under vacuum at elevated temperatures. The surface area increased by only 10–15%. The loss of carbon due to gasification during the reaction varied from 15 to 25%, depending upon the initial oxygen content of the material. The product was highly acidic, the base adsorption capacity being over 1200 m Eq/100 g. It was highly hydrophilic. Its capacity for moisture-adsorption at lower relative vapor pressures ($p/p_0 = 0.18$) was 10 to 12 times higher and its heat of immersion 6 to 7 times higher than the corresponding values of the original materials.

The reaction of activated carbons with chlorine water was examined by Behrman and Gustafson (*83*) and Puri et al. (*96,97*). The reaction takes place in two stages. The first stage involves conversion of chlorine into hydrochloric acid and chemisorption of a part of the oxygen, rendered available by the charcoal (*96*). After some time when charcoal is not in a position to chemisorb any more oxygen, the reaction involves formation of hydrochloric and chloric acids, charcoal acting merely as a catalyst (*97*).

$$3Cl_2 + 3H_2O \rightarrow 5HCl + HClO_3$$

The oxygen content of a sugar charcoal, outgassed at 1200°C which was originally free of oxygen, could be raised to 25% on repeated treatments with chlorine water at room temperature.

Reactions with aqueous sodium hypochlorite, leading to the formation of phenolic and carboxylic groups have been reported by Donnet (*98–100*), Boehm (*101*), Kiselev (*102*), and Mukherjee (*103*). Reactions with aqueous potassium persulfate, bromate, periodate, and nitrate have been reported by Puri, Mahajan, and Singh (*104*), and by Donnet (*105*).

Reactions with aqueous ferric chloride were studied in detail by Puri and Mahajan (*106*). The kinetics for the reduction of ferric ions obeyed an equation of the second order. The rate of the reaction at room temperature was shown to be extremely slow. The temperature coefficient of the reaction between 25° and 70°C was found to be close to two. The oxygen rendered available was partly chemisorbed and partly consumed up in causing gasification. The capacity of the charcoal for the reaction depended upon its capacity to utilize oxygen in gasification. The original charcoals already coated with oxygen complexes were more readily gasified and were therefore better reductants than the outgassed charcoals.

3. Slow pick-up of oxygen on aging

The effect of aging on oxygen content was studied (*107*) more directly by exposing various portions of chars, obtained by carbonizing cane sugar and coconut shells at various temperatures between 350° and 600°C, to dry air, humid air, and oxygen at room temperature. The chars continued to pick up oxygen slowly from air but rapidly from oxygen. Thus, although in oxygen the process was completed in 12 hr, in air it took almost 3 months for completion. The presence of moisture had very little effect on the rate of pick-up. Ultimately, the same value for oxygen content, characteristic of the charcoal and the temperature of carbonization, was obtained in every case. The increase in the oxygen content was about 3% in sugar charcoal and 1.7% in coconut charcoal, if these had been carbonized at 350°C. The values were appreciably less if they had been carbonized at higher temperatures. Most of the new oxygen was found to come off as carbon dioxide on thermal decomposition in vacuum. There was considerable increase in surface acidity of charcoal on aging in every case.

C. Decomposition of Carbon–Oxygen Surface Complexes

The surface oxygen complexes formed on treatment of carbons with oxygen or oxidizing gases are generally stable, even under high vacuum, at all temperatures below the temperature of formation. But regardless of the method of formation, they are generally stable to about 250°C. When outgassed around this temperature, the gas evolved consists mostly of carbon dioxide and water vapor. There is very little carbon monoxide. Around 500°C, however, the evolution of carbon monoxide also commences and with increasing temperatures the ratio CO_2/CO continuously decreases. Above 600°C, the gas evolved is largely carbon monoxide. Hydrogen comes off as steam to about 500°C—occasionally to 700°C—and above that as the elementary gas.

Johnson (*108,109*) showed that the combined oxygen in carbon blacks comes off on evacuating slowly at 400°C and rapidly at 955°C in the form of carbon dioxide and carbon monoxide. Anderson and Emmett (*110,111*) heated a few samples of carbon blacks in vacuum at different temperatures and found the products to be water, carbon dioxide, carbon monoxide, and hydrogen. Most of the water vapor and carbon dioxide were given off at or below 600°C, while carbon monoxide was evolved primarily between 600° and 900°C, and hydrogen at 900°C and above.

Puri and co-workers (*107,112–114*) subjected a number of samples of charcoal and carbon blacks (previously outgassed to constant weight at 150°C) to vacuum pyrolysis at gradually increasing temperatures. The gases evolved were analyzed in the following sequence: Water was removed in calcium chloride tubes and carbon dioxide, in a series of Erlenmeyer flasks containing a known amount of barium hydroxide solution. Carbon monoxide and hydrogen, in the remaining gas, were estimated in an Orset–Lunge gas analysis apparatus in the usual way. The temperature of the furnace was allowed to rise gradually and, before it was raised by 50°C, it was ensured that the gas had been completely eliminated at the lower temperature.

The significance of gradually raising the temperature lay in the fact that carbon dioxide, the evolution of which commenced even in the 200°–300°C temperature range, was absorbed in baryta solution as soon as it formed and thus escaped reduction to carbon monoxide at the higher temperatures. Similarly, the chemisorbed water was removed at much lower temperatures ($<$500°C) to minimize the chances of its interacting with carbon at higher temperatures. The usual size of the sample was about one gram. The time required for evacuation at a particular temperature varied from 1 to 5 hr, depending upon the temperature of evacuation and the oxygen content of the sample. The evolution of carbon dioxide was found to commence in the 200°–300°C temperature range and to end in the 700°–800°C temperature range. The evolution of carbon monoxide commenced in the 500°–700°C range and ended around 1000°C. The evolution of water, like that of carbon dioxide, commenced in the 200°–300°C temperature range and ended in the comparatively lower temperature range of 400–500°C. Only traces were evolved at higher temperatures. The liberation of free hydrogen was detected in small quantities around 500°–700°C. It came off in large quantities in the region of 700°–1000°C. An appreciable amount of hydrogen, representing in some cases as much as 25–35% of the total, was retained by the carbons even when outgassed at 1200°C.

Caltharp and Hackerman (*115*) conducted a thermal decomposition of the complexes on Spheron-6 by passing a stream of purified helium over a sample of the black which had been predried at 150°C. The samples varied from 5 to 12 g. The minimum time required for complete elimination of the major gas constituents at any temperature was 40 hr. This unusually long time was probably due to the large size of the sample. The gases evolved were separated and measured manometrically. The differential decomposition patterns were obtained by plotting the amount evolved in a given temperature interval against that interval. The plots for carbon dioxide indicated 300°–700°C as the main region of appearance, with the maximum at 500°–600°C. For carbon monoxide, 400°–800°C was the main region of appearance with the maximum at 600°–700°C. The features of the decomposition pattern of carbon dioxide, with regard to the range and the location of the maximum were different for Spheron-6 from those for Mogul-A (*114*), Graphon (*46*), and a charcoal, CWSN-S5 (*110*), reported by other workers. The features of the decomposition pattern for carbon monoxide, however, were the same for all the carbons mentioned above.

In a number of carbon blacks of different types the total amount of oxygen evolved—as carbon dioxide, carbon monoxide, and water vapor—after thermal pyrolysis at 1200°C was shown (*114*) to be in fair agreement with the total oxygen obtained by ultimate analysis (*65*). The difference was well within the limit of error to be expected from two such dissimilar methods. The total hydrogen evolved as water vapor and free hydrogen, however, was found to be less than the value obtained by ultimate analysis. The difference, representing nearly 25–35% of the total, was retained by the samples outgassed at 1200°C. This hydrogen, probably dispersed within the interior of the particles, required a much higher temperature to eliminate it.

Pyrolysis studies conducted on charcoals and carbon blacks indicate that the oxygen complexes are of more than one type and that the composition of the evolved gas, at a particular temperature, depends on the type and the amount of the complex decomposing at that temperature. There are also indications that there are definite surface groups which evolve carbon dioxide, and similarly there are distinct entities responsible for the evolution of carbon monoxide or water vapor. It has been suggested (*40,116,101*) that carbon dioxide is derived from carboxylic groups and their derivatives such as lactones, while carbon monoxide is mainly a decomposition product of quinones, hydroquinones, and phenols. Water appears to come from hydroquinones and phenols.

The oxygen content in furnace blacks varies generally between 0.2 and 1.3%, in channel blacks, between 3 and 3.5%, and in color blacks, between 4 and 8% (*114*). The fraction of the oxygen evolved as carbon dioxide (i.e., as CO_2 complex) has been found to be about 15% in channel blacks and about 30% in color blacks. The higher value in color blacks appears to be due to their exposure to air during formation, at 400°C, which is known to be the optimum temperature for the formation of the CO_2 complex (*22,23*). The channel blacks which are exposed to air at higher temperatures of around 600°C contain a much smaller proportion of this complex, as could be expected because the complex is not stable at this temperature. The total oxygen content in most of the furnace blacks, which are produced at much higher temperatures, is too low to show really what significant proportion of it is evolved as carbon dioxide.

The relationship between total oxygen (*114*) and nitrogen surface (*65*) is shown graphically in Fig. 1. The samples of different varieties are seen to fall on separate lines, indicating 9, 25, and 30 mg of oxygen/100 m² of the surface for furnace, channel, and color blacks, respectively.

Similar relationships for the oxygen present as CO_2 complex and that present as CO complex are shown in Figs. 2 and 3, respectively. It is seen that as far as the CO_2 complex is concerned, channel blacks rank with furnace blacks in having a smaller value (3 mg/100 m²), while the color blacks have a much higher value (6 mg/100 m²). As far as the CO complex

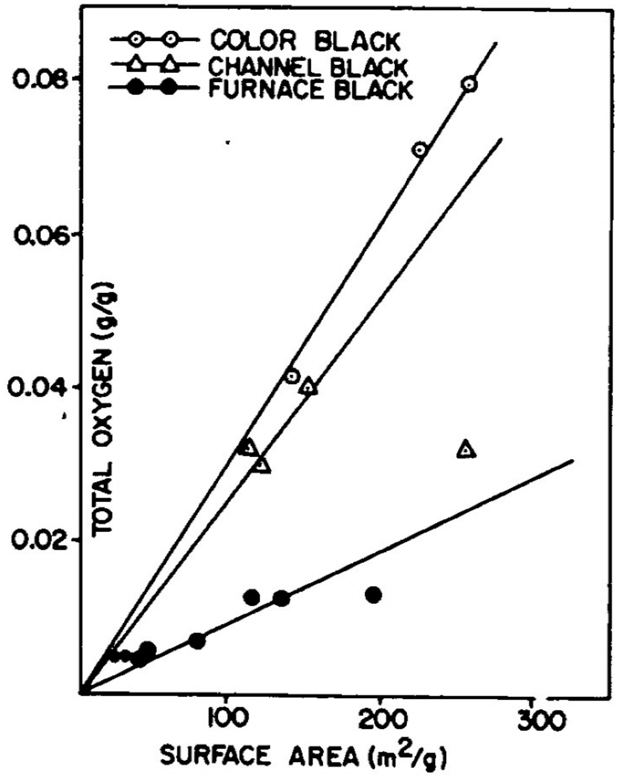


Fig. 1. Relation between total oxygen and surface area of carbon blacks.

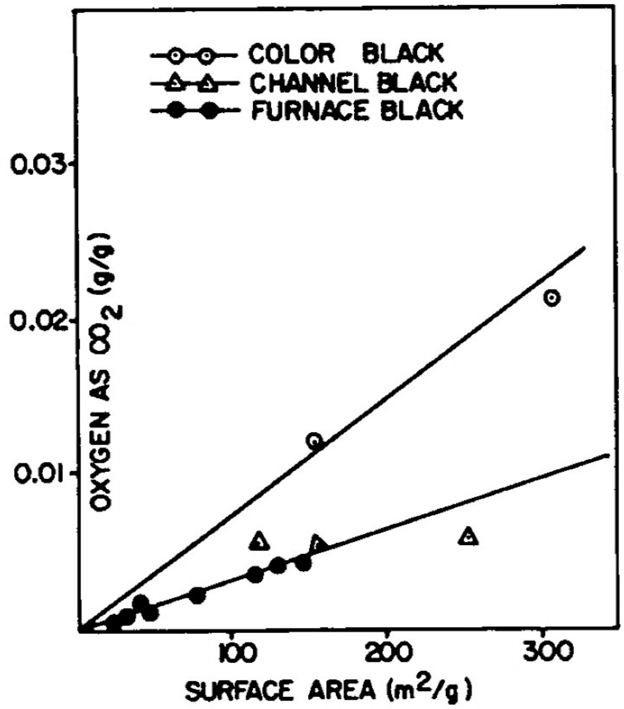


Fig. 2. Relation between oxygen evolved as carbon dioxide and surface area of carbon blacks.

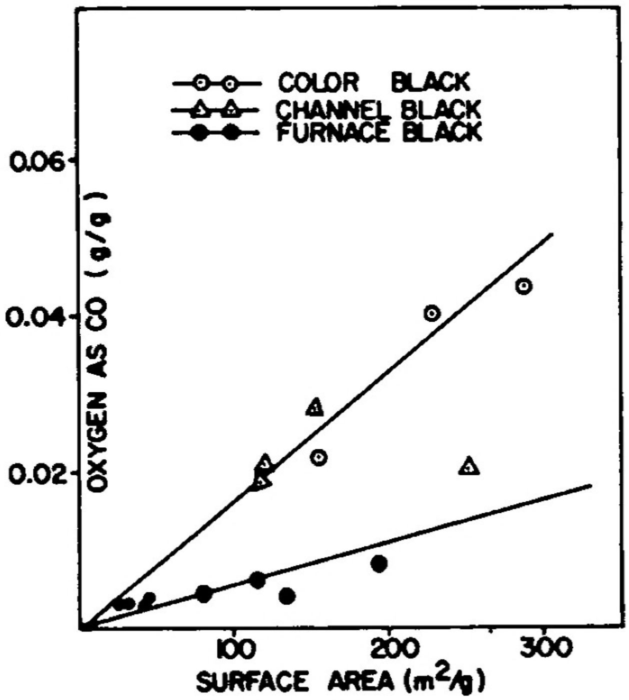


Fig. 3. Relation between oxygen evolved as carbon monoxide and surface area of carbon blacks.

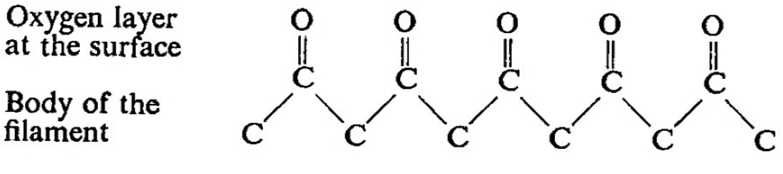
is concerned, channel blacks rank with color blacks in having a higher value, around 16 mg/100 m^2, while furnace blacks have a very low value, of around 5 mg/100 m^2. This is to be expected because air treatment at 600°C, to which channel blacks are subjected, takes away much of the CO_2 complex, without appreciably affecting the CO complex. Thus the amount and nature of surface–oxygen complexes vary considerably with the history of formation of the carbons.

In the case of charcoals also the amount of CO_2 complex is known to decrease appreciably with increase in the carbonization temperature beyond 400°C, while the amount of the CO complex remains almost unchanged or decreases only slightly on raising the temperature up to 600°C (*112*).

Smith et al. (*63*) heated their carbons in a current of hydrogen at 1000°C to remove carbon–oxygen complexes and to obtain clean carbon surfaces. Puri, Kumar, and Singh (*117*) showed that the treatment of charcoals in a current of hydrogen at 600°C for 16 hours causes complete elimination of oxygen as well as partial elimination of hydrogen. There were no indications in these experiments of reformation of the complexes on mere exposure to air at room temperature. Some later work, however, indicates formation of a small amount of oxygen complex with Graphon. Lobenstein and Deitz (*28*) showed that treatment of bone char with hydrogen at 400°C results in enhanced chemisorption of oxygen at 200°C and concluded that the hydrogen treatment causes formation of covalent C—H bonds. Emmett (*67*) observed an increase in surface area of carbons when treated with hydrogen analogous to what happens on treatment with steam or carbon dioxide. According to him, the two processes are similar because in both cases carbon atoms are lost from the surface, producing methane when hydrogen is passed and oxides of carbon when steam is passed, resulting in surface etching.

D. Hypothetical Structures

Several hypothetical structures and formulas have been assigned to carbon–oxygen surface complexes. Langmuir (*119*), for example, assuming each oxygen atom to be chemically bonded to a surface carbon atom, assigned the following structure:



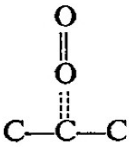
This hypothesis afforded an easy explanation of the extraordinary difficulty in removing oxygen from carbons. When the filament was heated with carbon dioxide at 1700°K, carbon monoxide was formed. The total volume, however, remained almost constant, showing that the reaction was not

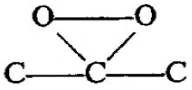
$$\underset{\text{(gas)}}{CO_2} + \underset{\text{(solid)}}{C} \rightarrow 2CO$$

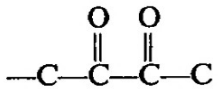
but was rather

$$\underset{\text{(gas)}}{CO_2} + \underset{\text{(solid)}}{C} \rightarrow \underset{\text{(gas)}}{CO} + \underset{\text{(surface complex)}}{(CO)}$$

Blench and Garner (*120*) and Garner (*121*) suggested the existence of three different surface oxides on charcoal because the adsorbed oxygen was found to be liberated in three different forms, i.e., as oxygen, as carbon monoxide, and as carbon dioxide. Garner and McKie (*16*), assuming that the interaction between carbon and oxygen takes place according to a stoichiometric relationship, suggested the following structural forms of the complexes:

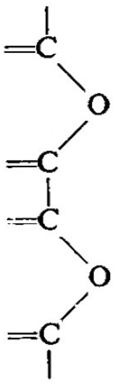

I

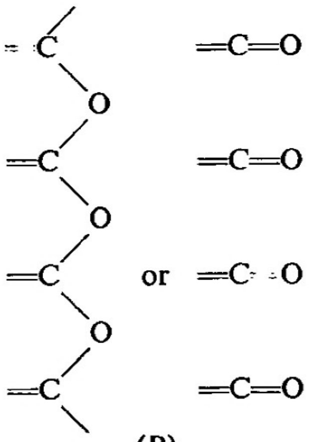

II

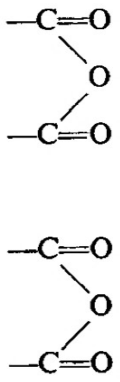

III

Formula I represents the process of physical adsorption in which there is no electron transference or sharing between the atoms. Adsorption, in this case, is reversible and oxygen can be recovered unchanged. Structures II and III represent the process of chemical combination. Structure II evolves carbon dioxide and structure III evolves carbon monoxide on heating.

Shilov et al. (*122*), in order to explain adsorption of acids and bases by carbons, suggested the existence of three different surface oxides.


(A)


(B)


(C)

A and B were supposed to be alkaline, and C acidic. The presence of acidic oxide was supported by Lepin (*14*) but the existence of alkaline oxides was questioned by Burnstein, Frumkin, and Lavrowskaja (*123*). The formation of yet another type of oxygen complex, formed at 950°C in the presence of oxidizing gases, was suggested by King (*124*).

Several workers have attempted to extract oxidized coals and charcoals with different reagents in order to get some clue to the nature and composition of the oxygen complexes. Using sulfuric acid as the extracting liquid, King (*125*,*126*), Kolthoff (*127*), and King and Lawson (*128*,*129*) recovered a small amount of an acid solution from ash-free charcoal activated with steam and oxygen. This substance was considered to be oxalic acid as it could reduce potassium permanganate. Bunte and Brückner (*130*) also observed formation of oxalic acid on pit coals. Peters and Cremer (*131*) could extract an acid substance from oxidized charcoal which reduced permanganate but could not be confirmed as oxalic acid. Lamb and Elder (*132*) extracted a small amount of a peroxide from a steam-activated charcoal. This substance was considered to be responsible for the catalytic properties of charcoal. Similarly, diphenyl oxide, 2,6-xylenol, and *p*-phenylphenol have been extracted in trace quantities from coals, using pyridine and ethylenediamine as the extracting liquids.

Puri et al. (*117*), during treatment of charcoals with hydrogen at 200°C, recovered a small amount of an acid substance, believed to be formic acid, formed probably by the interaction of elementary hydrogen with the decomposition products of the oxygen complexes.

The amounts of the various compounds recovered by the extraction processes have been extremely small and have furnished no useful information regarding the nature of the surface-oxygen complexes.

E. Acid-Base Character of Carbons in Relation to Chemisorbed Oxygen

A good deal of information, although of speculative nature, regarding the structure of surface oxides has been forthcoming from data on adsorption of acids and bases by carbons. It has been known for sometime that the acidic or basic character of a carbon depends upon its history of formation and, in particular, upon the temperature at which it has been heated. Wiegand (*133*), for instance, showed that aqueous suspensions of color blacks, which are heated in air at a temperature around 400°C during formation, give low pH values in the acid range, while those of furnace blacks, which are formed at considerably higher temperatures, give high pH values in the alkaline range. The suspensions of channel blacks, which are obtained at intermediate temperatures (around 600°C), give pH values lying in between the two extreme ranges. King (*134*) reported that charcoal activated in air or oxygen at a particular temperature has a specific pH value characteristic of that temperature. Singh, Sharma, and Puri (*135*) showed that the pH value of sugar charcoal in aqueous suspension, which was close to 3, increased as the charcoal was outgassed at increasing temperatures. It increased close to 7 at 750°C and rose further to about 8.6 at 1000°C.

Carbons outgassed at high temperatures and exposed to oxygen between 200° and 700°C have been shown (*22,38*) to adsorb appreciable amounts of strong bases but very little of strong acids. The optimum temperature for the development of maximum capacity to adsorb bases has been shown to lie close to 400°C. This temperature is also optimum for the maximum fixation of oxygen (*22,23*), as already mentioned in Section II.B. This fact led some workers (*23*) to think that the base adsorption capacity of a carbon is closely related to its oxygen content. This view has not been substantiated, as will be shown later in this section.

On the other hand, if outgassed carbons are exposed to oxygen either below 200°C or above 700°C they adsorb strong acids but very little strong bases. There is no definite temperature range, however, within which exposure to oxygen results in exclusive development of acid character and outside of which it results in exclusive development of basic character. Actually, there is a certain overlap of temperature where one type of character starts declining and the other type starts rising. Base adsorption capacity of a carbon, however, when it is acidic in nature, is far in excess of its acid-adsorption capacity, when it is basic in character.

Kruyt and de Kadt (*136*) showed that the electrokinetic potential of acidic carbons is negative whereas that of basic carbons is positive. Bennister and King (*137*) and Puri, Singh, and Sandle (*138*), however, were not able to prepare positively charged carbons. This may be due to their failure to prevent contact of the carbons with air during cooling after outgassing at high temperatures.

Frumkin and co-workers (*139,140*) explained adsorption of acids but not of bases by charcoals activated in air at 950° to 1000°C. As reported by Miller and co-workers (*141–143*), this is due to the presence of oxygen which becomes associated with the charcoal during the activation process. This charcoal, according to them, behaves as an oxygen electrode, like a spongy platinum electrode, yielding hydroxyl ions at the expense of the adsorbed oxygen when brought in contact with water or an aqueous solution. This reaction can be represented by the following equation:

$$C_xO + H_2O \rightarrow C_x + 2OH^- + 2^+$$