INTRODUCTION
INTRODUCTION

Broadly speaking, there are two distinct types of adsorption at solid-gas interface. One of these arises from a weak interaction between a solid surface and a gas, involving purely physical, that is, van der Waals forces, as in the case of a simple condensation of a gas. This is known as physical adsorption. The second type occurs on account of exchange or sharing of electrons between a solid surface and a gas, and the forces involved are valency or chemical forces, as in a chemical reaction. This is known as chemisorption. Physical adsorption is non-specific and, in general, occurs between all solids and all gases, while chemisorption is specific to a given pair, as it can occur only if some sort of chemical interaction is possible. Physical adsorption is reversible as the adsorbate can be easily recovered by altering conditions of temperature and pressure, while chemisorption is irreversible since the adsorbate cannot be recovered by any simple means. In chemisorption, the chemisorbed layer is only one molecule thick because the adsorbate molecules are linked to the surface atoms by valency forces. In physical adsorption, on the other hand, adsorbate molecules may form a monolayer or a multilayer,
the later possibility arises at pressures close to the saturation pressure of the adsorbate.

The most obvious distinction between physical adsorption and chemisorption is that while in the former case, the enthalpy change (heat of adsorption) is of the same order of magnitude (8-10 Kcals/mole) as that of condensation of a gas, in the latter case, the enthalpy change is much higher and is of the same order of magnitude (20-200 Kcals/mole) as that in a chemical reaction. Another criterion for distinguishing between physical adsorption and chemisorption, as suggested by Kipling and Peakaal(94,95), is that in the case of physical adsorption the adsorbate can be completely recovered at the same temperature, and a slight rise in temperature causes an immediate decrease in the amount of the substance adsorbed, whereas in the case of chemisorption, the adsorbate cannot be recovered at the same temperature and a slight increase in temperature has little or no effect on the amount of adsorption.

One of the earliest examples of chemisorption was furnished by Langmuir during his work on the interaction of oxygen with filaments of carbon (115) and tungsten (116) at high temperatures. The gas was held so firmly that it came off as oxides of carbon and tungsten on heating. Some other cases of chemisorption, reported in the early literature, are
oxygen on silver (16) and gold (17), carbon monoxide and oxygen on manganese dioxide and cupric oxide (85), carbon monoxide on tungsten (116), hydrogen and carbon monoxide on zinc oxide and chromium oxide mixtures (67), and hydrogen and water vapour on graphite (9). The study of chemisorption at solid-gas interface has assumed considerable importance in recent years as it helps in understanding not only the mechanism of surface reactions but also that of heterogeneous catalysis.

Chemisorption on carbons has formed the subject matter of a number of investigations in recent years. The surface carbon atoms, particularly those located at the edges or other active sites, due to residual valency forces have a strong tendency to 'chemisorb' or 'fix' atoms of other elements. Many of the surface reactions of carbons arise either because of this tendency to chemisorb other elements or because of the existence of a superfacial layer of chemically bonded elements. For example, it is well known that charcoals and carbon blacks (frequently referred to as microcrystalline carbons) can chemisorb oxygen on mere exposure to air (46, 60, 104, 143, 164) or oxygen (125, 194, 224), preferably at 400-500° (122, 133, 172, 204, 235, 239), giving rise to, what are commonly known as, carbon-oxygen surface complexes. The oxygen is held so firmly that it comes off only as oxides of carbon on high temperature evacuation (5, 6,
Carbon can also chemisorb nitrogen on treatment with ammonia (15, 24, 38, 83, 84, 153, 192, 211, 212), sulphur on treatment with hydrogen sulphide (142, 211, 212), carbon disulphide (210, 216) or sulphur (24, 209, 237, 246, 247), chlorine on treatment with the gas (2, 24, 180, 182, 188, 205), and bromine on treatment with the halogen in gaseous (181) or solution phase (157, 166), giving rise to stable, carbon-nitrogen, carbon-sulphur, carbon-chlorine and carbon-bromine surface complexes. It is also well known that almost all the carbons contain chemically bonded hydrogen (6, 8, 199, 231) which is so firmly held that it is not given off completely even on outgassing at 1200°C (6). Carbons are also known to chemisorb certain molecular species and free radicals such as water (161), methanol (158), formic acid (93), polynitro compounds (210), and quinones (210), etc.

The carbon-oxygen surface complexes are known to be formed more readily than the other complexes. In fact, it is now well recognised that these complexes are invariably present on microcrystalline carbons (11, 130, 183, 184, 185, 186, 206) and, in some cases, are of such great importance that many of the reactions which appear seemingly those of the carbons, are in reality those of the complexes themselves. The formation and properties of the surface oxygen complexes, therefore, have been studied by many workers in recent years and chemisorption of oxygen on carbons is perhaps the most
extensively investigated case of chemisorption. There is evidence to believe that in carbons, the fraction which exists in the form of disordered single stacked layers is more susceptible, while the fraction which shows some degree of well ordered parallel stacking is least susceptible to chemisorption of oxygen or other gases or vapours. There are more exposed defects and dislocations in the layer planes of microcrystalline carbons, than in crystalline carbons, and these 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, possess large internal and external surface areas per unit weight, respectively. These materials, therefore, although not so well defined as the graphites are of greater interest from the point of view of chemisorption studies.

**Formation of carbon-oxygen surface complexes**

Direct treatment of carbon in a current of oxygen at various temperatures was used by a number of workers, including Lowry and Huellett (126), Bartell and Miller (11), Garner and McKie (68), Shilov et al (193, 194, 195), Almond and Chaplin (3), Lepin (120), King (87), Weller and Young (235), Wilson and Bolas (239), Puri et al (164, 165, 172), Snow et al (204), Walker et al (111, 224, 228, 231, 232), Donnet et al (51, 52) and Boehm et al (23) for the formation of carbon-oxygen
surface complexes. Weller and Young (235) and Wilson and Bolam (239) studied chemisorption of oxygen on charcoal and at different pressures and were able to build up oxide layers containing 18 and 16.5 per cent oxygen at a temperature of 400°. Puri et al (165) studied chemisorption of oxygen on completely outgassed charcoals and found that the optimum temperature for the chemisorption of oxygen was 400°. On outgassing, the chemisorbed oxygen was given off as carbon dioxide, carbon monoxide and water vapour. Watt and Franklin (234), using ozonised oxygen, were able to build up an oxide layer containing as much as 40 per cent oxygen. Snow et al (204) treated a few carbon black samples with oxygen at different temperatures up to 400°, and from analytical, oxidation and X-ray data concluded that the solid carbon-oxygen complexes, that result from the treatment, contain appreciably more disorganised matter than the original carbon black. The activation energy of the process was estimated to be about 25-30 Kcals/g. atom of carbon oxidised. The oxygen was found to be fixed on the deep surface as well as 10-20 Å into the interior of the carbon. The surface area increased appreciably during oxidation. Loebenstein and Deitz (122), while studying the interaction of oxygen with a few carbon samples including bone charcoal, coconut shell charcoal and channel blacks, at 200°, concluded that only a part of the oxygen used was chemisorbed and the
rest was used for combustion. According to Deitz and McFarlane (37), who examined the oxidation of high surface area carbon films with oxygen at temperatures varying from 100-300°C, the oxygen was chemisorbed rapidly in the beginning and slowly afterwards. The slow step was believed to be a reaction between molecular oxygen and surface carbon atoms. The activation energy of the reaction varied between 16 and 35 Kcals/mole as the amount of oxygen chemisorbed increased from 1 to 6 moles of oxygen per film.

Walker et al. (111, 224, 228, 231, 232), in a series of publications, have shown that the treatment of carbon blacks and graphites with oxygen at various temperatures up to 635°C results in the formation of gaseous carbon dioxide, carbon monoxide and carbon-oxygen surface complexes. These complexes decompose to give carbon dioxide and carbon monoxide on thermal treatment. Donnet and Pappier (51, 52) studied oxidation of Philblack-O with oxygen in the temperature range 100-300°C and found that the optimum temperature for the chemisorption of oxygen was 100°C. They observed that the oxidation occurred mostly on the amorphous part of the carbon, and that it caused granulation and formation of oxygen-containing functional groups, resulting in an increase in the capacity of carbon black for reacting with free radicals. Medalia et al. (132), Barp and Hill (58) and Thomas (220) also noted chemisorption of oxygen by carbon
blacks on treatment with oxygen. Chemisorption of oxygen on graphite has been investigated by Lyons et al (128), Herring et al (80), Parker and Hottel (139), Kutcha et al (109) and Lang (114); and that on diamond powder by Barrer (12), Boehm (25) and Evans and Phhaal (61).

Other gases, such as oxides of nitrogen (4, 13, 129, 190, 191, 200, 202, 207, 208), carbon dioxide (19, 20, 27, 36, 77, 173, 179, 221, 229, 230) and water vapour (18, 75, 124, 196, 197, 208, 230, 231, 236, 238) have also been used for the oxidation of carbon surface. Shah (190, 191) reported the formation of an adsorption complex of oxygen at charcoal surface on treatment with nitrous and nitric oxides. This was shown to be an important preliminary step in the combustion of charcoal. Strickland-Constable (207, 208), and later on Madalay and Strickland-Constable (129), also observed chemisorption of oxygen by charcoal on treatment with nitrous oxide at 300°. Smith, Lessini and Mook (200) studied the interaction of nitrous oxide with graphon, a carbon black, and sugar charcoal, in 300-400° temperature range. They found that the reaction was of the first order and involved, at first, a rapid oxidation of the active centres on the carbon surface, resulting in the formation of carbon-oxygen surface complexes, and nitrogen, followed by a slow reaction in which the complexes were oxidised to gaseous carbon dioxide, and more nitrogen was produced.
Smith, Swineheart and Lessini (202) studied the interaction of nitric oxide with graphon and sugar charcoal and postulated that a nitric oxide molecule reacts with another adsorbed at the site of an oxygen complex to give nitrogen, carbon-dioxide, and an oxygen complex on the adjacent carbon atom. The new oxygen complex usually served as a site for further adsorption and thus the reaction was continued. Puri et al (171) studied the interaction of nitrogen dioxide with sugar and coconut shell charcoals at temperatures varying from 100-600° and found that the treatment resulted in the formation of carbon-oxygen surface complexes—the optimum temperature being 400°. It has been shown that the complexes formed by oxygen and nitrogen dioxide are identical in nature, as indicated by their similar decomposition products (171), and nearly equal heats of formation (171).

Tonge (221), while studying carbon-carbon dioxide reaction, observed that a surface oxide was formed during the reaction. Similar observations have also been made by Deitz et al (36), Walker et al (229, 230) and Lang et al (113). According to Harker et al (77) and Reif (179), carbon dioxide oxidises carbon to carbon monoxide, forming oxygen complexes as intermediates—the various stages of the reaction being:

\[
\text{CO}_2 + C \xrightarrow{\text{fast}} \text{CO} + (\text{CO}) \text{ oxygen complex}
\]
The interaction of carbons with water vapour has also been studied by many workers. Smith, Pierce and Joel (201) treated a few samples of carbon black with water vapour in the temperature range 25 - 100°C and found that the treatment resulted in the formation of a hydrogen complex and two types of oxygen complexes, one decomposing to give carbon dioxide and the other carbon monoxide, on heating. Puri et al (196), while studying the interaction of superheated steam with sugar charcoal at temperatures upto 1000°C, also observed the formation of oxygen complexes. However, Studebaker (213), on treating carbon black in a dynamic system in wet air and wet nitrogen, observed chemisorption of hydrogen only and not that of oxygen. The results were explained by postulating that carbon blacks adsorbed water molecules with dissociation and retained hydrogen preferentially.

A number of inorganic oxidants in aqueous solution have also been used for surface oxidation of carbons. The interaction between potassium permanganate and carbons has been studied fairly extensively. Behrman and Gustafson (14) observed that manganese dioxide was also formed during
the reaction. Winslow (240) observed that the presence of chemisorbed oxygen considerably impaired the capacity of the carbon for the reaction and concluded that surface oxygen complexes consist of peracidic rather than peroxidic groups which reduce permanganate. Garten and Weiss (71) suggested oxidation of chromenes to lactones during interaction. Bannerjee, Mazumdar and Lahiri (10) showed that permanganate, whether acidic or alkaline, reacts vigorously with coal even at room temperature until the coal is reduced to water-soluble products. Puri, Sharma and Mahajan (176) also studied the interaction of acidified potassium permanganate with sugar and coconut shell charcoals and observed that the oxygen rendered available during the reaction was partly chemisorbed and partly utilised for gasification of the charcoal to carbon dioxide. The interactions of charcoal and carbon blacks with nitric acid and nitric acid-sulphuric acid mixtures have also been studied by several workers. The treatments result in the chemisorption of oxygen (83, 177, 217) and, according to some workers, in the formation of functional groups such as carboxylic (110), phenolic (47), quinonic (72) and the free radicals (45). According to Puri et al (177), the oxygen chemisorbed by sugar charcoal during the reaction gives rise to a surface complex capable of evolving carbon dioxide on decomposition and that the treatment renders the
surface hydrophilic and causes formation of extremely fine micropores. The heat of immersion in water also increases considerably. The chemisorption of oxygen on treatment of carbon with aqueous sodium hypochlorite, leading to the formation of functional groups, such as phenolic hydroxyl and carboxylic, has been reported by Kiselev et al (102), Donnet (41,43,44), Boehm et al (23), and Mukherjee (136). Other oxidising agents in aqueous solution such as hydrogen peroxide (28,63,65,87,117,168,189), silver salts (176), halogens (14,155,170), ferric chloride (72,152,223) ammonium persulphate (23), potassium persulphate, bromate, iodate, nitrate (40,143,156) and dichromate (48,135) are also known to be reduced by carbons resulting in the chemisorption of oxygen.

Structure of carbon-oxygen surface complexes

Several hypothetical structures and formulae have been assigned to carbon-oxygen surface complexes. Langmuir(115), for example, assuming each oxygen atom to be chemically combined with a surface carbon atom, assigned the following structure to the oxygen complex capable of evolving carbon monoxide on thermal decomposition.

oxide layer
body of the filament
Bleach and Garner (21) and Garner (66) suggested the existence of three different types of surface oxides on charcoal because the adsorbed oxygen was liberated in three forms, namely, oxygen, carbon monoxide and carbon dioxide. Garner and McKie (68) assuming that the interaction between carbon and oxygen takes place according to definite stoichiometric relationship, suggested the following simple structural forms for the complexes.

\[
\begin{align*}
&\text{(I)} & &\text{(II)} & &\text{(III)} \\
&\text{C} & &\text{C} & &\text{C} \\
&\text{O} & &\text{O} & &\text{O}
\end{align*}
\]

Formula (I) represents the process of physical adsorption while structures (II) and (III) represent the processes of chemical combination. Structure (II) evolves carbon dioxide, while structure (III) evolves carbon monoxide on thermal decomposition. Shilov et al (193, 194, 195), in order to explain adsorption of acids and bases by charcoals, suggested the existence of three different oxides on charcoal surface.

\[
\begin{align*}
&\text{(A)} & &\text{(B)} & &\text{(C)} \\
&\text{C} & &\text{C} & &\text{C} \\
&\text{O} & &\text{O} & &\text{O} \\
&\text{O} & &\text{O} & &\text{O} \\
&\text{or} & &\text{or} & &\text{or}
\end{align*}
\]
(A) and (B) were supposed to be alkaline while (C) was supposed to be acidic. The existence of acidic oxide was confirmed by Lepin (120), but the existence of alkaline oxide was questioned by Burstein, Frumkin and Lawrowskaja (31).

Recently, many workers have attempted to carry out a more direct analysis of the surface oxide layer using methods based on organic reactions, infrared spectroscopy and polarographic and potentiometric techniques for identification and estimation of various functional groups. Villars (225), for instance, reacted some carbon blacks with Grignard's reagent, and from the amount of methane evolved, concluded that about 20 per cent of combined oxygen in carbon blacks can be accounted for as carboxylic or phenolic oxygen. Smith and Schaeffer (203) desorbed the oxide layer with fast moving neutrons and adduced evidence for the existence of (-OH), (-CO), (-COOH) and (-CH<sub>2</sub>) groups, from the study of emission spectra. Hoffman and Ohlerich (83) methylated two samples of sugar charcoal, one essentially free of oxygen and the other rich in oxygen, and from subsequent methoxy group determinations, concluded that large amounts of carboxylic and phenolic groups were present on the surface of charcoal sample rich in oxygen.

Studebaker et al (214) treated a number of carbon blacks with diazomethane solution in dry ether and estimated
the methoxy contents of treated samples, before and after hydrolysis with dilute hydrochloric acid. The hydrolysable and non-hydrolysable methoxy groups were attributed to the methylation products of carboxylic and phenolic groups, respectively. The increase in nitrogen content during the treatment was attributed to the presence of 1:4-quinones. These workers also estimated the quinonic oxygen by other methods such as hydrogen uptake from sodium borohydride (123) and catalytic hydrogenation with Adam's catalyst, and concluded that nearly 33 per cent of the total oxygen in carbon blacks was in the form of quinonic groups. Garten and Weiss (69) were of the view that carbons acquired a quinonic structure when oxidised and hydroquinonic structure when reduced. Later on, Garten, Weiss and Willis (70), after making a detailed study of the various reactions of activated charcoals and carbon blacks, attributed the acidity of carbons to the presence of three functional groups, phenols, lactones of fluoresce type (f-lactone), and normal lactones. According to them the hydrolysable methoxy groups formed during diazomethane treatment do not arise from carboxylic groups, as had been suggested by other workers (83,214), but from f-lactones. Their objection to the presence of carboxylic groups was based on the fact that the titration curves of charcoals obtained by Villars (226) and of carbon blacks,
(obtained by themselves (72). With strong alkalies, did not indicate the presence of acid groups of such high strength. Garten and Weiss (71) also examined the basic nature of carbons activated at high temperatures and attributed the acid adsorption to the presence of oxygen-containing chromene groups.

Donnet et al (43-53) oxidised a number of carbon blacks with air, ozone, hydrogen peroxide, sodium hypochlorite, sodium chromate, potassium permanganate, potassium dichromate and nitric acid, and studied the functional groups present on the surface of oxidised carbons by chemical reactions as well as by infrared spectra. They adduced (43) evidence for the presence of functional groups such as carboxylic, phenolic and quinonic groups on the surface of oxidised carbon blacks. According to them, free radicals as well as quinone groups exist in an aroxyl form. Puri and Bedi (147) have also shown the presence of quinone groups on sugar and coconut shell charcoals, by treating them with hydrogen gas at 160° and measuring the increase in acidity thus produced. In this reaction, it was assumed that the quinone groups were reduced to hydroquinone structures with phenolic character.

Recently, Boehm et al (23), who studied oxidation of activated charcoals and carbon blacks with oxygen, potassium permanganate and ammonium persulphate, have shown
that acidity developed on the oxidised samples was due to the formation of four acidic functional groups: (i) strongly acidic carboxylic groups which can be neutralised by weak alkalies like sodium bicarbonate, (ii) lactone groups which can be neutralised by a relatively stronger alkali like sodium carbonate, (iii) phenolic hydroxyl groups which can only be neutralised by a strong alkali like sodium hydroxide, and (iv) carbonyl groups which can react with sodium ethoxide. These workers supported their views by carrying out various organic reactions. Rivin (187) estimated the active hydrogen on the surface of a number of carbon blacks by treating them with lithium aluminium hydride and measuring the hydrogen evolved. He employed the selective neutralisation technique similar to that employed by Boehm et al (23) to distinguish between the various acidic groups. Yamida and Suzuki (245) adduced evidence for the presence of carboxylic and quinonic groups using methylation and potentiometric techniques. Mizitouri et al (134) also estimated acidic carboxylic and hydroxylic groups on a number of carbon black samples, and found that the relative amounts of these groups differed widely in the various carbon blacks.

Infrared absorption spectra of carbons has also been studied by many workers. Brown (29) and Friedel and Queiser (64), during their studies on coals and other
carbonacious materials, observed an absorption band at 1600 cm\(^{-1}\) which they attributed to the presence of phenolic hydroxyl groups. Garten, Weiss and Willis (70) also observed absorption bands at 1600 cm\(^{-1}\) and 1750 cm\(^{-1}\), which they attributed to the presence of phenolic and lactonic groups, respectively. Cole and Dannenberg (32) also studied infra-red spectra of various carbon blacks and observed absorption bands at 4.3 and 6.3 microns in the case of every carbon black. They attributed the band at 6.3 to an extremely stable structure, believed to be a conjugated chelate resulting from the interaction between beta-situated ketonic groups and/or beta situated hydroxy and ketonic structures. However, it was pointed out by Studebaker (210) that this band may be due to the presence of carboxylate ions (chemisorbed carbon dioxide or carboxyl ions) as was previously reported by Eischen (59) for chemisorbed carbon dioxide on nickel. The other band at 4.3 microns was attributed by these workers to the presence of adsorbed carbon dioxide.

Hallum and Drushell (76) during their studies of infra-red spectra of methylated carbon blacks, observed a distinct absorption band at 1750-1700 cm\(^{-1}\) together with a weak absorption band at 1240 cm\(^{-1}\) which was not shown initially by the carbon black. Since the first band is associated generally with normal carbonyl group and the latter with
methoxy group, it was concluded that originally, the carbonyl groups had been chelated to phenolic hydroxyl groups through hydrogen bonding. These observations were confirmed by carrying out polarographic analysis of carbon blacks suspended in dimethyl formamide using tetra-n-butylammonium iodide as a supporting electrolyte. Half-wave potentials, characteristic of quinones, appeared at the cathode and disappeared on treatment with lithium aluminium hydride. Half wave potentials, characteristic of hydroquinones, appeared at the anode and disappeared on treatment with hydrogen peroxide or diazomethane. These workers proposed the following models for structures investigated by them.

Donnet and Henrich (45) also observed a half wave potential, characteristic of quinones, in the cathodic polarogram of an oxidised carbon black. The wave disappeared on treatment of the carbon with isobutyronitrile which is known to react with quinones.

Although the existence of various functional groups, such as carboxyls, carbonyls, phenols, lactones, quinones,
hydroquinones and chromenes has been suggested as discussed above, the methods used for their estimation have not yielded comparable results and, what is even more significant, the entire oxygen has not been accounted for (30). The applicability of organic reactions to the surface of carbons has been questioned by several workers. According to Boehm et al (24), the functional groups present on graphite crystallites react with organic reagents only slowly and incompletely. The chances of complete reaction between organic reagents and surface groups on carbon blacks and charcoals would be far less due to essential heterogeneity of the reaction system. All such reactions can be hindered by stereochemical and porosity effects. The infrared spectra can also be of limited help, as has been pointed out by several workers (72, 98, 198). It is difficult to get a good absorption spectra due to continued background absorption (72) and also due to the fact that the various functional groups may not be present as simple, independent non-associated structures and the wide absorption band can be interpreted in more than one ways.

According to Puri et al (146, 162, 163, 172), the acidity of carbons is entirely due to the presence of an oxygen complex capable of evolving carbon dioxide on thermal decomposition, which they have termed as CO₂ complex. They regard base adsorption as a neutralising reaction (162, 172).
They suggest that charcoal or carbon black, by virtue of the presence of \( \text{CO}_2 \)-complex in its surface oxide layer, is capable of undergoing surface ionisation in water, furnishing \( \text{H}^+ \) ions (and thus behaves as a weak colloidal acid or acidoid) as represented below:

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_3^{2-} + 2\text{H}^+
\]

The surface hydrogen ions, being directed towards the liquid phase, can bring about neutralisation of alkalies in stoichiometric amounts, as shown below:

\[
\text{CO}_3^{2-} + 2\text{H}^+ + 2\text{MOH} \rightarrow \text{CO}_3^{2-} + 2\text{M}^+ + 2\text{H}_2\text{O}
\]

Puri et al. found further evidence in support of their view from measurements of heats of neutralisation (148) which were very close to those for neutralisation of carbonic acid by the same alkali as well as from electrometric and conductometric titration (174) which resembled closely those of carbonic acid.

Influence of surface oxygen complexes on the surface behaviour of carbons.

It appears from the literature cited above that the various structures and formulae proposed for the surface
oxygen complexes are yet to be established and that there are many divergent views on the subject. But, whatever be the exact mechanism by which the oxygen atoms are bound to the surface carbon atoms and whatever be the exact structure or composition of the oxide layer, it is known from X-ray examination and other data that these atoms or groups are present mainly at the edges of giant molecules forming layer planes. As these edges constitute the main adsorbing surface, the combined oxygen exercises a profound influence on the surface behaviour and surface reactions of carbons. For instance, it is now well established that the acidity of carbons is entirely due to the presence of combined oxygen, although there are divergent views as to the structure and nature of the groups responsible for this property, as has been pointed out earlier in this chapter. Many surface reactions of carbons are known to be influenced by combined oxygen. For example, Winslow (240) and recently Puri and Mahajan (151) observed that the presence of chemisorbed oxygen decreased the capacity of charcoal to reduce potassium permanganate. According to Lamb and Elder (112), the catalytic activity of carbons for the oxidation of ferrous ions in acid solution by molecular oxygen was about 200 times more surface in the presence of oxygen-containing groups than that in their absence. Feigl (62), who studied catalytic oxidation of some
inorganic salts in the presence of charcoal, observed that the catalytic activity of charcoal was due to the presence of a film of adsorbed oxygen. According to Puri et al (169), who studied the catalytic oxidation of aqueous solutions of sodium nitrite, potassium arsenite, sodium sulphite and potassium ferrocyanide in the presence of sugar charcoals, the catalytic activity of charcoal is enhanced by the presence of the oxygen complex capable of evolving carbon dioxide (CO₂-complex). However, the presence of this complex was found to decrease the activity of charcoal for the decomposition of hydrogen peroxide (168) as well as for the combination of hydrogen and bromine (149).

The presence of chemisorbed oxygen is known to increase the hydrophilic character of carbons. The low temperature oxidation of ink, colour and lamp blacks, is, therefore, often used to improve their hydrophilic character. Studebaker and Snow (215) measured contact angle, θ, of a number of carbon blacks by a modification of Wolkova's method (241) and found that cos θ, which is a measure of wettability, was a function of oxygen and hydrogen contents.

The effect of surface oxides on the sorption of water vapour has been investigated by many workers. Lawson (119), King and Lawson (89), Kiselev (101), Emmett (60), Dubinin and Zaverina (54-57), Healey et al (79), McDermott and
Arnell (131), Anderson and Emmett (5) and Pierce et al (140) have shown that the presence of chemisorbed oxygen increases the sorption of water vapour at low pressures. Pierce, Smith, Wiley and Cordes (140) showed that the water isotherms of graphon changed materially after exposure to water vapour at 80°C. The difference was attributed to interaction of water vapour with graphon producing a carbon-oxygen surface complex which adsorbed water more readily than the clean carbon surface. Pierce and Smith (139), and Dubinin, Zaverina and Serpinski (57), have shown that the adsorption of water vapour first takes place on certain hydrophilic sites provided by the oxygen complexes, in the form of isolated 'clusters'. These 'clusters' then grow in size, as more adsorption takes place on adsorbed water molecules, till ultimately they merge to form a continuous layer. The forces between water molecules which were confined to the isolated points now extend over the whole layer, as a result of which the adsorbed layer becomes stabilized. The hysteresis arises from the fact that whereas the adsorption occurs at the isolated hydrophilic sites, the desorption occurs from the stabilised continuous layers (in the case of non-porous carbons) or the menisci (in the case of porous carbons) formed on account of merger of the isolated clusters at higher relative pressures. McDermot and Arnell (131) removed oxygen from three types of charcoals by treating them with hydrogen, and observed that the
removal of oxygen resulted in decrease of water sorption at all relative humidities up to 80 per cent. The original capacity to adsorb water vapour was found to be largely restored when these samples were 

oxidised on exposure to water vapour for 3 months at 60°C. These workers also supported the 'cluster' theory of hysteresis. Puri et al (161) observed that it is not the total combined oxygen, but only that part of it which comes off as carbon dioxide (CO₂-complex), that influences water vapour adsorption.

A certain amount of water adsorbed on charcoals containing CO₂-complex could not be desorbed even on evacuating the system at the temperature of adsorption and was regarded as fixed by a mechanism involving hydrogen bonding. The amount of such water was found to correspond roughly to one mole of water per mole of CO₂-complex. Adsorption of methyl alcohol (158) and ethyl alcohol (159) was also observed to be influenced by the presence of CO₂-complex in the same manner.

Selective adsorption by carbons from binary liquid solutions has also been shown to be influenced by the presence of carbon-oxygen surface complexes. Kipling et al (33,73,74, 91,92,96,97), Kiselev et al (99,100,103,105), Wright (242, 243,244), Abram (1), Craig (34) and Ulazova (222) have shown that the presence of chemisorbed oxygen imparts polar
character to the carbon surface and promotes selective adsorption of polar liquids. Puri et al. (150) observed that while the presence of CO$_2$-complex enhances the adsorption of polar substances, that of CO-complex enhances the adsorption of aromatic substances from binary solutions. Cation exchange properties of carbons have also been attributed to the presence of carboxylic or phenolic groups (198, 218) and to the presence of the oxygen complex capable of evolving carbon dioxide (154). Kraus (108) observed that the heat of immersion of carbon blacks in water and non-aqueous solvents depended on the amount of chemisorbed oxygen. Puri et al. (173), have shown that the heat of immersion in water depends mostly on the amount of CO$_2$-complex. According to them, this complex imparts polar nature and hydrophilic character to the carbon surface. Dispersibility (53), wettability (42), and electrical properties (210) of carbons have also been shown to be affected by chemisorbed oxygen.

Scope of the present work

It appears from the above perusal of the literature that the problem of carbon-oxygen surface complexes has not been properly elucidated so far. This is true not only with regard to the number, nature and structure of the surface oxides but also with regard to the conditions of their
formation and the exact influence which they exercise on surface behaviour of carbons. There is need, therefore, to investigate further the conditions of formation of these complexes and to study the surface behaviour and surface reactivities of carbons coated with different oxygen-complexes in order to understand the exact manner in which these complexes play such an important role in altering the various surface characteristics.

The adsorbent carbons selected in the present investigations were charcoals and carbon blacks. The charcoals were prepared by the carbonisation of cane sugar and coconut shells. These were freed of ash in order to avoid any extraneous influence. The ash-free charcoals were used as such, and are referred to in the text as 'original' charcoals. These samples were also outgassed at different temperatures upto 1000°C. These samples are referred to, in the text, as 'outgassed' charcoals and are prefixed by the temperature at which they were outgassed. The carbon blacks used were of well known commercial varieties and were received as gift from Mr. M.L. Studebaker of the Philips Petroleum Company, U.S.A.

The thesis has been divided into six chapters followed by a separate part giving full details of the experimental techniques and methods used in the investigations.

The first chapter deals with the nature of the surface oxides present on the various samples of charcoal and carbon
black. For this purpose certain specific chemical reactions were carried out, for the estimation of various functional groups. Potentiometric titration curves, using different alkalies, were also determined with a view to understand the nature of the groups responsible for surface acidity.

The second chapter deals with the chemisorption of oxygen by charcoals and carbon blacks, differing in their initial oxygen contents, on treatment with various oxidising gases and solutions, and a study of the nature of the surface complexes formed in each case.

The next chapter describes the effect of extensive oxidation, using increasing amounts of various oxidising solutions, on gasification as well as formation of surface complexes responsible for acidity of carbon.

The succeeding chapters deal with the influence of carbon-oxygen surface complexes on the surface behaviour of carbons. The fourth chapter, for instance, describes the effect of the various oxygen complexes on the adsorption of water, methanol and benzene vapours on some samples of charcoal and carbon black.

The next chapter describes the effect of carbon-oxygen surface complexes on heats of immersion in water and other non-aqueous solvents while the last chapter deals with the effect of
these complexes on adsorption from binary liquid mixtures of non-electrolytes.

A summary of the conclusions arrived at from these investigations has been given at the end of the thesis.


171. Puri, B.B., Singh, D.D., Kumar, P. and Sharma, L.R.,

172. Puri, B.B., Singh, D.D., Nath, J. and Sharma, L.R.,


238. Wicke, E. and Rossberg, M., Primary and secondary reaction in the gasification of coal with steam. Z. Elektrochem., 57, 641 (1953).


***************