# Activated Carbon Adsorption



## Roop Chand Bansal Meenakshi Goyal



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CRC Press Taylor & Francis Group 6000 Broken Sound Parkway NW, Suite 300 Boca Raton, FL 33487-2742

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International Standard Book Number-13: 978-1-4200-2881-2 (eBook - PDF)

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## Preface

Activated carbons are versatile adsorbents. Their adsorptive properties are due to their high surface area, a microporous structure, and a high degree of surface reactivity. They are, used, therefore, to purify, decolorize, deodorize, dechlorinate, separate, and concentrate in order to permit recovery and to filter, remove, or modify the harmful constituents from gases and liquid solutions. Consequently, activated carbon adsorption is of interest to many economic sectors and concern areas as diverse as food, pharmaceutical, chemical, petroleum, nuclear, automobile, and vacuum industries as well as for the treatment of drinking water, industrial and urban waste water, and industrial flue gases.

Interest in activated carbon adsorption of gases and vapors received a big boost during and after the first World War, while an increasing attention to the activated carbon adsorption from aqueous solutions was initiated by the pollution of the environment, which includes air and water, due to rapid industrialization and everincreasing use of the amount and the variety of chemicals in almost every facet of human endeavor. Life has initiated increasing attention to the activated carbon adsorption from aqueous solutions. It was, therefore, thought worthwhile and opportune to prepare a text that describes the surface structure of activated carbons, the adsorption phenomenon, and the activated carbon adsorption of organics and inorganics from gaseous and aqueous phases.

A vast amount of research has been carried out in the area of activated carbon adsorption during the past four or five decades, and research data are scattered in different journals published in different countries and in the proceedings and abstracts of the International Conferences and Symposia on the science and technology of activated carbon adsorbents. This book critically reviews the available literature and tries to offer suitable interpretations of the surface-related interactions of the activated carbons. The book also contains consistent explanations for surface interactions applicable to the adsorption of a wide variety of adsorbates that could be strong or weak electrolytes.

The book has been written with a view to equip the surface scientists (chemists, physicists, and technologists) with the surface processes, their energetics, and with the adsorption isotherm equations, their applicability to and deviations from the adsorption data for both gases and solutions. To carbon scientists and technologists, the book should help understand the parameters and the mechanisms involved in the activated carbon adsorption of organic and inorganic compounds. The book thus combines in one volume the surface physical and chemical structure of activated carbons, the surface phenomenon at solid-gas and solid-liquid interfaces, and the activated carbon adsorption of gaseous adsorbates and solutes from solutions.

This unified approach will provide the reader access to the relevant literature and promote further research toward improving and developing newer activated carbon adsorbents and develop processes for the efficient removal of pollutants from drinking water and industrial effluents. The book can also serve as a text for studies relating to adsorption and adsorption processes occurring on solid surfaces.

The authors are grateful to Elsevier, Ann Arbor Science publishers, South African Institute of Mining and Metallurgy, Marcel Dekker Multi-Science Publishing Co., Society of Chemistry and Industry, and various authors for permission to reproduce certain figures and tables. Professor Bansal also acknowledges the understanding, the cooperation, and the encouragement of his wife Rajesh Bansal. Dr. Meenakshi Goyal is grateful to her husband Er. Arvinder Goyal for his patience and help, and to her son Nikhil and daughter Mehak, who accepted her extreme busyness and continued to attain excellence in their schools during the preparation of the manuscript. We also thank Tulsi Ram and Ruby Singh for typing the manuscript and preparing figures and tables.

> Roop Chand Bansal Meenakshi Goyal

### Introduction

#### ACTIVATED CARBONS

Activated carbon in its broadest sense includes a wide range of processed amorphous carbon-based materials. It is not truly an amorphous material but has a microcrystalline structure. Activated carbons have a highly developed porosity and an extended interparticulate surface area. Their preparation involves two main steps: the carbonization of the carbonaceous raw material at temperatures below 800°C in an inert atmosphere and the activation of the carbonized product. Thus, all carbonaceous materials can be converted into activated carbon, although the properties of the final product will be different, depending on the nature of the raw material used, the nature of the activating agent, and the conditions of the carbonization and activation processes.

During the carbonization process, most of the noncarbon elements such as oxygen, hydrogen, and nitrogen are eliminated as volatile gaseous species by the pyrolytic decomposition of the starting material. The residual elementary carbon atoms group themselves into stacks of flat, aromatic sheets cross-linked in a random manner. These aromatic sheets are irregularly arranged, which leaves free interstices. These interstices give rise to pores, which make activated carbons excellent adsorbents. During carbonization these pores are filled with the tarry matter or the products of decomposition or at least blocked partially by disorganized carbon. This pore structure in carbonized char is further developed and enhanced during the activation process, which converts the carbonized raw material into a form that contains the greatest possible number of randomly distributed pores of various sizes and shapes, giving rise to an extended and extremely high surface area of the product. The activation of the char is usually carried out in an atmosphere of air, CO<sub>2</sub>, or steam in the temperature range of 800°C to 900°C. This results in the oxidation of some of the regions within the char in preference to others, so that as combustion proceeds, a preferential etching takes place. This results in the development of a large internal surface, which in some cases may be as high as  $2500 \text{ m}^2/\text{g}$ .

Activated carbons have a microcrystalline structure. But this microcrystalline structure differs from that of graphite with respect to interlayer spacing, which is 0.335 nm in the case of graphite and ranges between 0.34 and 0.35 nm in activated carbons. The orientation of the stacks of aromatic sheets is also different, being less ordered in activated carbons. ESR studies have shown that the aromatic sheets in activated carbons contain free radical structure or structure with unpaired electrons. These unpaired electrons are resonance stabilized and trapped during the carbonization process, due to the breaking of bonds at the edges of the aromatic sheets, and

thus, they create edge carbon atoms. These edge carbon atoms have unsaturated valencies and can, therefore, interact with heteroatoms such as oxygen, hydrogen, nitrogen, and sulfur, giving rise to different types of surface groups. The elemental composition of a typical activated carbon has been found to be 88% C, 0.5% H, 0.5% N, 1.0% S, and 6 to 7% O, with the balance representing inorganic ash constituents. The oxygen content of an activated carbon can vary, however, depending on the type of the source raw material and the conditions of the activation process.

The activated carbons in general have a strongly developed internal surface and are usually characterized by a polydisperse porous structure consisting of pores of different sizes and shapes. Several different methods used to determine the shapes of the pores have indicated ink-bottle shaped, regular slit shaped, V-shaped, capillaries open at both ends, or with one end closed, and many more. However, it has been difficult to obtain accurate information on the actual shape of the pores. It is now well accepted that activated carbons contain pores from less than a nanometer to several thousand nanometers. The classification of pores suggested by Dubinin and accepted by the International Union of Pure and Applied Chemistry (IUPAC) is based on their width, which represents the distance between the walls of a slitshaped pore or the radius of a cylindrical pore. The pores in activated carbons are divided into three groups: the micropores with diameters less than 2 nm, mesopores with diameters between 2 and 50 nm, and macropores with diameters greater than 50 nm. The micropores constitute a large surface area (about 95% of the total surface area of the activated carbon) and micropore volume and, therefore, determine to a considerable extent the adsorption capacity of a given activated carbon, provided however that the molecular dimensions of the adsorbate are not too large to enter the micropores. The micropores are filled at low relative vapor pressure before the commencement of capillary condensation. The mesopores contribute to about 5% of the total surface area of the carbon and are filled at higher relative pressure with the occurrence of capillary condensation. Attempts, however, are now on to prepare mesoporous carbons. The macropores are not of considerable importance to the process of adsorption in activated carbons, as their contribution to surface area does not exceed 0.5 m<sup>2</sup>/g. They act as conduits for the passage of adsorbate molecules into the micro- and mesopores.

Because all the pores have walls, they will comprise two types of surfaces: the internal or microporous surface and the external surface. The former represents the walls of the pores and has a high surface area that may be several thousands in many activated carbons, and the latter constitutes the walls of the meso- and macropores as well as the edges of the outward facing aromatic sheets and is comparatively much smaller and may vary between 10 and 200 m<sup>2</sup>/g for many of the activated carbons.

Besides the crystalline and porous structure, an activated carbon surface has a chemical structure. The adsorption capacity of an activated carbon is determined by the physical or porous structure but strongly influenced by the chemical structure of the carbon surface. In graphites that have a highly ordered crystalline structure, the adsorption capacity is determined mainly by the dispersion component of the van der Walls forces. But the random ordering of the aromatic sheets in activated carbons causes a variation in the arrangement of electron clouds in the carbon skeleton and

results in the creation of unpaired electrons and incompletely saturated valencies, which would undoubtedly influence the adsorption properties of activated carbons. Activated carbons are invariably associated with certain amounts of oxygen and hydrogen. In addition, they may contain small amounts of nitrogen. X-ray diffraction studies have shown that these heteroatoms are bonded at the edges and corners of the aromatic sheets, or to carbon atoms at defect positions, giving rise to carbon-oxygen, carbon-hydrogen, and carbon-nitrogen surface compounds. As the edges constitute the main adsorbing surface, the presence of these surface compounds modifies the surface characteristics and surface properties of activated carbons.

Carbon-oxygen surface groups are by far the most important surface groups that influence the surface characteristics such as the wettability, polarity, and acidity, and the physico-chemical properties such as catalytic, electrical, and chemical reactivity of these materials. In fact, the combined oxygen has often been found to be the source of the property by which a carbon becomes useful and effective in certain respects. For example, the presence of oxygen on the activated carbon surface has an important effect on the adsorption capacity of water and other polar gases and vapors on their aging during storage, on the adsorption of electrolytes, on the properties of carbon blacks as fillers in rubber and plastics, and on the lubricating properties of graphite as well as on its properties as a moderator in nuclear reactors. In the case of carbon fibers, these surface oxygen groups determine their adhesion to plastic matrices and consequently improve their composite properties.

Although the identification and estimation of the carbon-oxygen surface groups have been carried out using several physical, chemical, and physio-chemical techniques that include their desorption, neutralization with alkalies, potential, thermometric, and radiometric titrations, and spectroscopic methods such as IR spectroscopy and x-ray photoelectron spectroscopy, the precise nature of the chemical groups is not entirely established. The estimations obtained by different workers using varied techniques differ considerably because the activated carbon surface is very complex and difficult to reproduce. The surface groups can not be treated as ordinary organic compounds because they interact differently in different environments. They behave as complex structures presenting numerous mesomeric forms depending upon their location on the same polyaromatic frame.

The aromatic sheets constituting the activated carbon structure have limited dimensions and therefore have edges. In addition these sheets are associated with defects, dislocations, and discontinuities. The carbon atoms at these places have unpaired electrons and residual valencies, and are richer in potential energy. These carbon atoms are highly reactive and are called active sites or active centers and determine the surface reactivity, surface reactions, and catalytic reactions of carbons. The impregnation of activated carbons with metals and their oxides, dispersed as fine particles, makes them extremely good catalysts for certain industrial processes. The impregnation of metals also modifies the gasification characteristics and varies the porous structure of the final product. Several inorganic and organic reagents when present on the carbon surface also modify the surface behavior and adsorption characteristics of activated carbons and make them useful for the removal of hazardous gases and vapors by chemisorption and catalytic decomposition.

#### Adsorption

Adsorption arises as a result of the unsaturated and unbalanced molecular forces that are present on every solid surface. Thus, when a solid surface is brought into contact with a liquid or gas, there is an interaction between the fields of forces of the surface and that of the liquid or the gas. The solid surface tends to satisfy these residual forces by attracting and retaining on its surface the molecules, atoms, or ions of the gas or liquid. This results in a greater concentration of the gas or liquid in the near vicinity of the solid surface than in the bulk gas or vapor phase, despite the nature of the gas or vapor. The process by which this surface excess is caused is called adsorption. The adsorption involves two types of forces: physical forces that may be dipole moments, polarization forces, dispersive forces, or short-range repulsive interactions and chemical forces that are valency forces arising out of the redistribution of electrons between the solid surface and the adsorbed atoms.

Depending upon the nature of the forces involved, the adsorption is of two types: physical adsorption and chemisorption. In the case of physical adsorption, the adsorbate is bound to the surface by relatively weak van der Walls forces, which are similar to the molecular forces of cohesion and are involved in the condensation of vapors into liquids. Chemisorption, on the other hand, involves exchange or sharing of electrons between the adsorbate molecules and the surface of the adsorbent resulting in a chemical reaction. The bond formed between the adsorbate and the adsorbent is essentially a chemical bond and is thus much stronger than in the physisorption.

Two types of adsorptions differ in several ways. The most important difference between the two kinds of adsorption is the magnitude of the enthalpy of adsorption. In physical adsorption the enthalpy of adsorption is of the same order as the heat of liquefaction and does not usually exceed 10 to 20 KJ per mol, whereas in chemisorption the enthalpy change is generally of the order of 40 to 400 KJ per mol. Physical adsorption is nonspecific and occurs between any adsorbate-adsorbent systems, but chemisorption is specific. Another important point of difference between physisorption and chemisorption is the thickness of the adsorbed phase. Although it is multimolecular in physisorption, the thickness is unimolecular in chemisorption. The type of adsorption that takes place in a given adsorbate-adsorbent system depends on the nature of the adsorbate, the nature of the adsorbent, the reactivity of the surface, the surface area of the adsorbate, and the temperature and pressure of adsorption.

When a solid surface is exposed to a gas, the molecules of the gas strike the surface of the solid when some of these striking molecules stick to the solid surface and become adsorbed, while some others rebound back. Initially the rate of adsorption is large because the whole surface is bare, but the rate of adsorption continues to decrease as more and more of the solid surface becomes covered by the adsorbate molecules. However, the rate of desorption, which is the rate at which the adsorbed molecules rebound from the surface, increases because desorption takes place from the covered surface. With the passage of time, the rate of adsorption continues to decrease, while the rate of desorption continues to increase, until an equilibrium is reached, where the rate of adsorption is equal to the rate of desorption. At this point the solid is in adsorption equilibrium with the gas. It is a dynamic equilibrium

because the number of molecules sticking to the surface is equal to the number of molecules rebounding from the surface.

As the amount adsorbed at the equilibrium for a given adsorbate-adsorbent system depends upon the pressure of the gas and the temperature of adsorption, the adsorption equilibrium can be represented as an adsorption isotherm at constant temperature, the adsorption bar at constant pressure, and the adsorption isostere for a constant equilibrium adsorption. In actual practice the determination of adsorption at constant temperature is most convenient and, therefore, the adsorption isotherm is the most extensively employed method for representing the equilibrium states of an adsorption system. The adsorption isotherm gives useful information regarding the adsorbate, the adsorbent, and the adsorption process. It helps in the determination of the surface area of the adsorbent, the volume of the pores, and their size distribution. It also provides important information regarding the magnitude of the enthalpy of adsorption and the relative adsorbility of a gas or a vapor on a given adsorbent with respect to chosen standards. The adsorption data can be represented by several isotherm equations, the most important being the Langmuir, the Freundlich, the Brunauer-Emmett-Teller (BET), and Dubinin equations. The first two isotherm equations apply equally to physisorption as well as to chemisorption. The BET and Dubinin equations are most important for the analysis of physical adsorption of gases and vapors on porous carbons.

The Langmuir isotherm equation is the first theoretically developed adsorption isotherm that was derived using thermodynamic and statistical approaches. The applicability of the equation to the experimental data was carried out by a large number of investigators, but deviations were often noticed. According to this isotherm equation, the plot of p/v against p should be linear from  $\theta = 0$  to  $\theta = \infty$ , and it should give a reasonable value of Vm (the monolayer capacity), which should be temperature independent. However, few data conform to this criterion. Similarly, several chemisorption results are known where the Langmuir equation is valid only within a small restricted range. Thus, although the Langmuir isotherm equation is of limited significance for the interpretation of the adsorption data because of its idealized character, the equation remains of basic importance for expressing dynamic adsorption equilibrium. Furthermore, it has provided a good basis for the derivation of other, more complex, models. The assumptions that the adsorption sites on solid surfaces are energetically homogeneous and that there are no lateral interactions between the adsorbed molecules are the weak points of this model.

Brunauer, Emmet, and Teller derived the BET equation for multimolecular adsorption by a method that is the generalization of the Langmuir treatment of unimolecular adsorption. These workers proposed that the forces acting in multimolecular adsorption are the same as those acting in the condensation of vapors. Only the first layer of adsorbed molecules, which is in direct contact with the adsorbent surface, is bound by adsorption forces originating from the interaction between the adsorbate and the adsorbent. Thus, the molecules in the second and subsequent layers have the same properties as in the liquid or gaseous phase. The BET equation has played a significant role in studies of adsorption because it represents the shapes of the actual isotherms. It also gives reasonable values for the average enthalpy of adsorption in the first layer and satisfactory values for Vm, the monolayer capacity of the adsorbate which can be used to calculate the specific surface area of the solid adsorbent.

The BET equation is applicable within the relative pressure range of 0.05 to 0.35. The failure of the equation above and below this range of relative pressures has been attributed to the faulty and simplifying assumptions of the theory. The failure below a relative pressure of 0.05 is due to the heterogeneity of the adsorbent surface. Activated carbon and inorganic gel surfaces that are important adsorbents are generally energetically heterogeneous (i.e., the enthalpy of adsorption varies from one part of the surface to another). At higher relative pressures, the BET equation loses its validity because adsorption by capillary condensation along with physical adsorption also takes place. The assumption that the adsorbate has liquidlike properties after the first layer is difficult to reconcile because both porous and nonporous adsorbents exposed to a saturated vapor sometimes adsorb strictly a limited amount and not the infinitely large quantity as postulated by the BET model. Thus, the limited validity of the BET equation is due to the shortcomings in the model itself rather than to our lack of knowledge of the various parameters, such as the number of layers, the heat of adsorption, or the evaporation constant in the higher layers.

The potential theory of adsorption and the Dubinin equation, which is based on it, have been developed primarily for microporous adsorbents, for which they have proved to be better than all other theories. Dubinin and coworkers, while investigating the effect of surface structure of activated carbons on the adsorbability of different vapors and of different solutes from solutions on active carbons, observed that over a wide range of values of adsorption, the characteristic curves of different vapors on the same adsorbent were related to each other. In fact, it was observed that if the adsorption potential corresponding to a certain volume of adsorption space on the characteristic curve for one vapor was multiplied by a constant, called the affinity coefficient, the adsorption potential corresponding to the same value of adsorption space on the characteristic curve of another vapor was obtained. Based on these observations, the characteristic curves for microporous activated carbons were expressed analytically by a Gaussian distribution equation between the total limiting volume of the adsorption space and the adsorption potential. This further made it possible to obtain an equation of the adsorption isotherm and to calculate the appropriate micropore volume. The Dubinin equation is valid over the range of relative pressures from  $1 \times 10^{-5}$  to 0.2 or 0.4, which corresponds to about 85 to 95% filling of the micropores. At relative pressures below 10<sup>-5</sup>, extremely ultra-fine micropores that are not accessible to larger molecules are filled. Thus, the potential theory of adsorption together with the Dubinin equation represent the temperature dependence of adsorption and enable calculation of important thermodynamic functions, such as the heat and entropy of adsorption. The Dubinin equation has been further modified by Kaganer to yield a method for calculating the specific surface area from these isotherms. He confined his attention to monolayer region and assumed that adsorption at very low relative pressures results in the formation of a unimolecular layer on the walls of all the pores. This method thus yields monolayer capacity rather than the micropore volume. The method is applicable in the low pressure region of the isotherm (below relative pressure of 10<sup>-4</sup>). The surface areas calculated by Kaganer method for activated carbons were within few percent of those calculated from the BET equation.

The Freundlich isotherm equation is a limiting form of the Langmuir isotherm and is applicable only in the middle ranges of vapor pressure. The equation is of greater significance for chemisorption, although some physical adsorption data have also been found to fit this equation.

Adsorption from solutions on activated carbons has wide applications in food, pharmaceutical, and other process industries to remove unwanted components from the solution. However, a theoretical analysis of adsorption from solution and the derivation of a suitable adsorption equation have been comparatively difficult because both the components of a solution compete with each other for the available surface. Furthermore, the thermal motion of the molecules in the liquid phase and their mutual interactions are much less well understood. It is, therefore, difficult to correctly assess the nature of the adsorbed phase, whether unimolecular or multimolecular. The adsorption of a solute from a solution is usually determined by the porosity and the chemical nature of the adsorbent, the nature of the components of the solution, the concentration of the solution, its pH, and the mutual solubility of the components in the solution. The adsorption of a nonpolar solute will be higher on a nonpolar adsorbent. But since there is competition between the solute and the solvent, the solvent should be polar in nature for the solute to be adsorbed preferentially. The other factor that also determines the adsorption from solutions is the steric arrangement or the chemical structure of the adsorbate molecule. As the activated carbons have a highly microporous structure, some of the pores may be inaccessible to larger molecules of the adsorbate. Thus, the experimentally simple technique of adsorption from solution can be developed into a method to determine surface area, microporosity, oxygen content, and the hydrophobicity of the carbon surface. The adsorption from solutions is also receiving further attention because of the growing importance of environmental control involving purification of waste water using activated carbons.

Adsorption from solutions can be classified into adsorption of solutes that have a limited solubility (i.e., from dilute solutions) and adsorption of solutes that are completely miscible with the solvent in all proportions. In the former case, the adsorption of the solvent is of little consequence and is generally neglected. In the latter case, the adsorption of both components of the solution plays its part and has to be considered. The adsorption in such a system is the resultant of the adsorption of both the components of the solution. The adsorption from such solutions is represented in the form of a composite isotherm, which is a combination of the isotherms for the individual components.

#### ACTIVATED CARBON ADSORPTION

Carbon surface has a unique character. It has a porous structure which determines its adsorption capacity, it has a chemical structure which influences its interaction with polar and nonpolar adsorbates, it has active sites in the form of edges, dislocations and discontinuities which determine its chemical reactions with other atoms. Thus, the adsorption behavior of an activated carbon can not be interpreted on the basis of surface area and pore size distribution alone. Activated carbons having equal surface area but prepared by different methods or given different activation treatments show markedly different adsorption properties. The determination of a correct model for adsorption on activated carbon adsorbents with complex chemical structure is therefore, a complicated problem. A proper model must take into consideration both the chemical and the porous structure of the carbon, which includes the nature and concentration of the surface chemical groups, the polarity of the surface, the surface area, and the pore size distribution, as well as the physical and chemical characteristics of the adsorbate, such as its chemical structure, polarity, and molecular dimensions. In the case of adsorption from solutions, the concentration of the solution and its pH are also important additional factors.

Thus, activated carbons are excellent and versatile adsorbents. Their important applications are the adsorptive removal of color, odor, and taste, and other undesirable organic and inorganic pollutants from drinking water, in the treatment of industrial waste water; air purification in inhabited spaces, such as in restaurants, food processing, and chemical industries; for the purification of many chemical, food, and pharmaceutical products; in respirators for work under hostile environments; and in a variety of gas-phase applications. Their use in medicine and health applications to combat certain types of bacterial ailments and for the adsorptive removal of certain toxins and poisons, and for the purifications of blood, is being fast developed. Activated carbons can be used in various forms: the powdered form, the granulated form, and now the fibrous form. Powdered activated carbons (PAC) generally have a finer particle size of about 44 µm, which permits faster adsorption, but they are difficult to handle when used in fixed adsorption beds. They also cause a high pressure drop in fixed beds, which are difficult to regenerate. The granulated activated carbon (GAC) have granules 0.6 to 4.0 mm in size and are hard, abrasion resistant, and relatively dense to withstand operating conditions. Although more expensive than PAC, they cause low hydrodynamic resistance and can be conveniently regenerated. GAC can be formulated into a module that can be removed after saturation, regenerated by heat treatment in steam, and used again. The fibrous activated carbon fibers (ACF) are expensive materials for waste water treatment, but they have the advantage of the capability to be molded easily into the shape of the adsorption system and produce low hydrodynamic resistance to flow.

The most important application of activated carbon adsorption where large amounts of activated carbons are being consumed and where the consumption is ever increasing is the purification of air and water. There are two types of adsorption systems for the purification of air. One is the purification of air for immediate use in inhabited spaces, where free and clean air is a requirement. The other system prevents air pollution of the atmosphere from industrial exhaust streams. The former operates at pollutant concentrations below 10 ppm, generally about 2 to 3 ppm. As the concentration of the pollutant is low, the adsorption filters can work for a long time and the spent carbon can be discarded, because regeneration may be expensive. Air pollution control requires a different adsorption setup to deal with larger concentrations of the pollutants. The saturated carbon needs to be regenerated by steam, air, or nontoxic gaseous treatments. These two applications require activated carbons with different porous structures. The carbons required for the purification of air in inhabited spaces should be highly microporous to affect greater adsorption at lower concentrations. In the case of activated carbons for air pollution control, the pores should have higher adsorption capacity in the concentration range 10 to 500 ppm. It is difficult to specify the pore diameters exactly, but generally in the micro- and meso- range are preferred because they fill in this concentration range.

The effluent gases from industry and processing units contain a large number of pollutants, such as oxides of nitrogen and sulfur,  $H_2S$ , and vapors of  $CS_2$ , styrene, and several solvents, such as ethanol or toluene. Many of these compounds can be economically recovered when present in large amounts. However, when present in low concentrations, these volatile organic compounds need to be removed from the flue gases before they are mixed with air. Activated carbon is one of the important adsorbents that are used for the recovery of useful compounds when economically viable and for adsorptive removal of the pollutant gases and vapors when present in small amounts. In addition, many of these VOCs are released from the exhaust of automobiles on the roads. In order to reduce this VOC release, catalyst converters are being used to convert VOC into  $CO_2$  and water vapors. The release of these VOCs can be further decreased by fitting the automobiles with activated carbon canisters. However, in addition to the porous structure of activated carbons, their surface chemistry is also of considerable interest.

For personal protection when working in a hostile environment, the activated carbons used in respirators are also different. When working in the chemical industry, the respirators can use ordinary activated carbons because the pollutants are generally of low toxicity. However, for protection against warfare gases such as chloropicrin, cynogen chloride, hydrocynic acid, and nerve gases, special types of impregnated activated carbons are used in respirators and body garments. These activated carbons can protect by physical adsorption, chemisorption, and catalytic decomposition of the hazardous gases.

More than 800 specific organic and inorganic chemical compounds have been identified in drinking water. These compounds are derived from industrial and municipal discharge, urban and rural runoff, natural decomposition of vegetable and animal matter, and from water and waste water chlorination practices. Liquid effluents from industry also discharge varying amounts of a variety of chemicals into surface and ground water. Many of these chemicals are carcinogenic and cause many other ailments of varying intensity and character. Several methods such as coagulation, oxidation, aeration, ion exchange, and activated carbon adsorption have been used for the removal of these chemical compounds. Many studies including laboratory tests and field operations have indicated that the activated carbon adsorption is perhaps the best broad spectrum control technology available at the present moment.

An activated carbon in contact with a salt solution is a two-phase system consisting of a solid phase that is the activated carbon surface and a liquid phase that is the salt solution containing varying amounts of different ionic and molecular species and their complexes. The interface between the two phases acts as an electrical double layer and determines the adsorption processes. The adsorption capacity of an activated carbon for metal cations from the aqueous solutions generally depends on the physico-chemical characteristics of the carbon surface, which include surface area, pore size distribution, electro-kinetic properties, the chemistry of the carbon surface, and the nature of the metal ions in the solution. Activated carbons are invariably associated with acidic and basic carbon-oxygen surface groups. The acidic groups that have been postulated as carboxyls, lactones, and phenols render the carbon surface polar and hydrophilic, and the basic groups have been postulated as pyrones and chromenes structures.

A perusal of the literature indicates that the more important parameters that influence and determine the adsorption of metal ions from aqueous solutions are the carbon-oxygen functional groups present on the carbon surface and the pH of the solution. These two parameters determine the nature and concentration of the ionic and molecular species in the solution. Electrokinetic studies have shown that the nature and concentration of the carbon surface charge can be modified by changing the pH of the carbon-solution system. The activated carbon surface has a positive charge below pH<sub>znc</sub> (zero point charge) and a negative charge above ZPC up to a certain range of pH values. The origin of the positive charge on the activated carbon surface has been attributed to the presence of basic surface groups, the excessive protonation of the surface at low pH values and to graphene layers that act as Lewis bases resulting in the formation of acceptor-donor complexes important for the adsorption of many organic compounds from aqueous solutions. At higher pH values, the carbon surface has a negative charge, due to the ionization of acidic carbonoxygen surface groups. Thus, the adsorption of metal ions mainly involves electrostatic attractive and repulsive interactions between metal ionic species in the solution and the negative sites on the carbon surface produced by the ionization of acidic groups. The dispersive interactions between the ionic species in the solution and the graphene layers and the surface area of the carbon surface play a smaller role in the adsorption of inorganics.

In the adsorption of organics, however, the situation is quite different. The organic compounds present in water can be polar or nonpolar, so that not only electrostatic interactions but also dispersive interactions will play an important role. In addition, the hydrogen bonding is also an important consideration in the adsorption of certain polar organic molecules. The molecular dimensions of the organic molecules also have a wide variation. Thus, the porous structure of the activated carbon, which includes the existence of mesopores, shall also have an important consideration for the adsorption of the microporosity may not be accessible to very large organic molecules.

This book has been written in eight chapters, which cover activated carbons; their surface structure; the adsorption on solid surfaces and the models of adsorption; adsorption from solution phase; the preparation, characterization of, and adsorption by carbon molecular sieves; important applications of activated carbons with special emphasis on medicinal and health applications; and the use of activated carbons in environmental clean up.

The crystalline, microporous, and chemical structures of the activated carbon surface are discussed in Chapter 1. This chapter discusses classification of pores and their contribution to surface area and adsorption capacity; the nature and characteristics of carbon-oxygen surface groups; the methods of their identification and estimation using physical, chemical, and physico-chemical methods, which include XPS and the latest innovations in infrared spectroscopy. Chapter 1 also delineates the influence of these surface groups on the adsorption characteristics and adsorption properties. The adsorption on a solid surface, the types of adsorption, the energetics of adsorption, the theories of adsorption, and the adsorption isotherm equations (e.g., the Langmuir equation, BET equation, Dubinin equation, Temkin equation, and the Freundlich equation) are the subject matter of Chapter 2. The validity of each adsorption isotherm equation to the adsorption data has been examined. The theory of capillary condensation, the adsorption-desorption hysteresis, and the Dubinin theory of volume filling of micropores (TVFM) for microporous activated carbons are also discussed in this chapter.

The adsorption from binary solutions on solid adsorbents in general and on activated carbons in particular is discussed in Chapter 3. The nature and types of adsorption and adsorption isotherms from dilute solutions and from completely miscible binary solutions are described. The composite isotherm equation is derived. The shapes and classification of composite isotherms and the influence of adsorbate-adsorbent interactions, the heterogeneity of the carbon surface, and the size and orientation of the adsorbed molecules on the shapes are examined. The thickness of the adsorbed layer and the determination of individual adsorption isotherms from a composite isotherm are also described.

Chapter 4 briefly describes the preparation of carbon molecular sieves by pore blocking of activated carbons by decomposition of  $H_2S$  or  $CS_2$ , and depositing sulfur, by decomposition of benzene or other hydrocarbons and deposition of carbon, and by impregnation of PVC followed by its decomposition. The characterization of carbon molecular sieves by molecular probe methods using adsorption of inorganic gases and organic vapors varying in size and shape and by immersional heats of wetting in liquids of varying sizes is discussed. The applications of CMS for the separation of different gaseous mixtures are also discussed.

Chapters 5 to 8 are devoted to important applications of activated carbon adsorption. The most general liquid phase and gas phase applications of activated carbons with special reference to the nature of the carbon surface and the form of the activated carbon are discussed in Chapter 5, with special emphasis on medicinal and health applications. Different types of carbons prepared from different source raw materials and using different activation treatments are examined for the control of drug overdose, control of antibacterial activities against certain bacteria to remove toxins and poisons from the human body, and for the purification of blood by hemoperfusion. The next two chapters are concerned with the adsorptive removal of inorganic (Chapter 6) and organic (Chapter 7) pollutants from drinking and waste waters. The various parameters that are involved in the removal of hazardous organics and inorganics are reviewed and the mechanisms involved are suggested. The subject matter of Chapter 8 is the adsorptive removal of hazardous gases and vapors from industrial flue gases and automobile exhaust. The use of activated carbon in respirators for work under hostile environments is also discussed.

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## 1 Activated Carbon and Its Surface Structure

Active carbon in its broadest sense is a term that includes a wide range of amorphous carbonaceous materials that exhibit a high degree of porosity and an extended interparticulate surface area. They are obtained by combustion, partial combustion, or thermal decomposition of a variety of carbonaceous substances. Active carbons have been obtained in granular and powdered forms. They are now also being prepared in spherical, fibrous, and cloth forms for some special applications. The granular form has a large internal surface area and small pores, and the finely divided powdered form is associated with larger pore diameters and a smaller internal surface area. Carbon cloth and fibrous activated carbons (activated carbon fibers) have a large surface area and contain a comparatively higher percentage of larger pores.

Active carbons in the form of carbonized wood charcoal have been used for many centuries. The Egyptians used this charcoal about 1500 BC as an adsorbent for medicinal purposes and also as a purifying agent. The ancient Hindus in India purified their drinking water by filtration through charcoal. The first industrial production of active carbon started about 1900 for use in sugar refining industries. This active carbon was prepared by the carbonization of a mixture of materials of vegetable origin in the presence of metal chlorides or by activation of the charred material by  $CO_2$  or steam. Better quality gas-adsorbent carbons received attention during World War I, when they were used in gas masks for protection against hazardous gases and vapors.

Active carbons are unique and versatile adsorbents, and they are used extensively for the removal of undesirable odor, color, taste, and other organic and inorganic impurities from domestic and industrial waste water, solvent recovery, air purification in inhabited places, restaurants, food processing, and chemical industries; in the removal of color from various syrups and pharmaceutical products; in air pollution control from industrial and automobile exhausts; in the purification of many chemical, pharmaceutical, and food products; and in a variety of gas-phase applications. They are being increasingly used in the field of hydrometallurgy for the recovery of gold, silver, and other metals, and as catalysts and catalyst supports. They are also well known for their applications in medicine for the removal of toxins and bacterial infections in certain ailments. Nearly 80% (~300,000 tons/yr) of the total active carbon is consumed for liquid-phase applications, and the gas-phase applications consume about 20% of the total production.

Because the active carbon application for the treatment of waste water is picking up, the production of active carbons is always increasing. The consumption of active carbon is the highest in the U.S. and Japan, which together consume two to four times more active carbons than European and other Asian countries. The per capita consumption of active carbons per year is 0.5 kg in Japan, 0.4 kg in the U.S., 0.2 kg in Europe, and 0.03 kg in the rest of the world. This is due to the fact that Asian countries by and large have not started using active carbons for water and air pollution control purposes in large quantities.

Carbon is the major constituent of active carbons and is present to the extent of 85 to 95%. In addition, active carbons contain other elements such as hydrogen, nitrogen, sulfur, and oxygen. These heteroatoms are derived from the source raw material or become associated with the carbon during activation and other preparation procedures. The elemental composition of a typical active carbon is found to be 88% C, 0.5% H, 0.5% N, 1% S, and 6 to 7% O, with the balance representing inorganic ash constituents. The oxygen content of the active carbon, however, may vary between 1 and 20%, depending upon the source raw material and the history of preparation, which includes activation and subsequent treatments. The most widely used activated carbon adsorbents have a specific surface area on the order of 800 to 1500 m<sup>2</sup>/g and a pore volume on the order of 0.20 to 0.60 cm<sup>3</sup>g<sup>-1</sup>. The pore volume, however, has been found to be as large as 1 cm<sup>3</sup>/g in many cases. The surface area in active carbons is predominantly contained in micropores that have effective diameters smaller than 2 nm.

Active carbons are mainly and almost exclusively prepared by the pyrolysis of carbonaceous raw material at temperatures lower than 1000°C. The preparation involves two main steps: carbonization of the raw material at temperatures below 800°C in an inert atmosphere, and activation of the carbonized product between 950 and 1000°C. Thus, all carbonaceous materials can be converted into active carbons, although the properties of the final product will be different, depending upon the nature of the raw material used, the nature of the activating agent, and the conditions of the activation process. During carbonization most of the noncarbon elements such as oxygen, hydrogen, nitrogen, and sulfur are eliminated as volatile gaseous products by the pyrolytic decomposition of the source raw material. The residual elementary carbon atoms group themselves into stacks of aromatic sheets cross-linked in a random manner. The mutual arrangement of these aromatic sheets is irregular and, therefore, leaves free interstices between the sheets, which may become filled with the tarry matter or the products of decomposition or at least blocked partially by disorganized carbon. These interstices give rise to pores that make active carbons excellent adsorbents. The char produced after carbonization does not have a high adsorption capacity because of its less developed pore structure. This pore structure is further enhanced during the activation process when the spaces between the aromatic sheets are cleared of various carbonaceous compounds and disorganized carbon. The activation process converts the carbonized char into a form that contains the largest possible number of randomly distributed pores of various shapes and sizes, giving rise to a product with an extended and extremely high surface area.

The preparation of active carbons from different source raw materials and using different techniques, their porous and surface chemical structures, have been discussed in details in the book *Active Carbon*.<sup>1</sup> Because this book is concerned more with active carbon adsorption, a brief discussion about the more important aspects of active carbon surface chemistry are covered in this book.

#### 1.1 CRYSTALLINE STRUCTURE OF ACTIVATED CARBONS

Active carbons have a microcrystalline structure that starts to build up during the carbonization process. However, the active carbon microcrystalline structure differs from that of graphite with respect to the interlayer spacing, which is 0.335 nm in the case of graphite and ranges between 0.34 and 0.35 nm in active carbons. The orientation of the microcrystallite layers is also different, being less ordered in active carbons. Biscoe and Warren<sup>2</sup> proposed the term *turbostratic* for such a structure. This disorder in microcrystallite layers is caused by the presence of heteroatoms such as oxygen and hydrogen, and by the defects such as vacant lattice sites in active carbons. The three-dimensional structure of graphite and the turbostratic structure of active carbon<sup>3</sup> are compared in Figure 1.1.

Franklin,<sup>4</sup> on the basis of his x-ray studies, classified active carbons into two types, based on their graphitizing ability. The nongraphitizing carbons, during carbonization, develop strong cross-linking between the neighboring randomly oriented elementary crystallites, resulting in the formation of a rigid immobile mass. The charcoals obtained are hard and show a well-developed microporous structure that is preserved even during the subsequent high-temperature treatment. In the case of PVDC (polyvinylidene chloride) charcoal, which is an example of a nongraphitizing carbon, about 65% of the carbon was arranged in graphitic layers of a mean diameter of 16Å.<sup>4</sup> The remaining carbon was highly disordered, 55% of the graphitic layers being grouped in pairs of parallel planes 0.37 nm apart. The average distance between elementary crystallites is approximately 2.5 nm. The PVDC charcoal does not graphitize even at temperatures higher than 3000°C. The formation of the nongraphitizing



**FIGURE 1.1** Comparison of three-dimensional crystal lattice of graphite (a) and the turbostratic structure (b). (After Bokros, J.C. in *Chemistry and Physics of Carbon*, Vol. 5, Marcel Dekker, New York, 1969. With permission.)



**FIGURE 1.2** Schematic illustration of the structure of active carbon: (a) easily undergoing graphitization and (b) undergoing graphitization to a small degree. (After Franklin, R.E., *Proc. Roy. Soc.*, A209, 196, 1951. With permission.)

structure with strong cross-links is promoted by the presence of associated oxygen or by an insufficiency of hydrogen in the original raw material.

In the case of PVC (polyvinyl chloride) charcoal, which is an example of a graphitizing carbon, Franklin observed that the elementary crystallites were mobile and had weak cross-linking from the beginning of the carbonization process. The charcoal obtained was weak and had a less-developed porous structure, but the crystallites had a large number of graphitic layers oriented parallel to each other. Franklin observed that, after the elimination of the nonorganized carbon, the growth of the crystallites continued, probably by the addition of layers or even groups of layers. The schematic representating the structures of graphitizing and nongraphitizing active carbons are shown in Figure 1.2.

The difference in abilities to undergo graphitization results from the difference in the orientation of the crystallites in the two types of carbons.

#### 1.2 POROUS STRUCTURE OF THE ACTIVE CARBON SURFACE

Active carbons with a random arrangement of microcrystallites and with a strong cross-linking between them have a well-developed porous structure. They have relatively low density (less than 2 gm/cm<sup>3</sup>) and a low degree of graphitization. This porous structure formed during the carbonization process is developed further during the activation process, when the spaces between the elementary crystallites are cleared of tar and other carbonaceous material. The activation process enhances the volume and enlarges the diameters of the pores. The structure of the pores and their pore size distribution are largely determined by the nature of the raw material and the history of its carbonization. The activation also removes disorganized carbon, exposing the crystallites to the action of the activating agent and leads to the development of a microporous structure. In the latter phase of the reaction, the widening of existing pores and the formation of large pores by burnout of the walls between the adjacent pores also takes place. This causes an increase in the transitional porosity and macroporosity, resulting in a decrease in the micropore volume. According to

Dubinin and Zaverina,<sup>5</sup> a microporous active carbon is produced when the degree of burn-off is less than 50% and a macroporous active carbon when the extent of burn-off is greater than 75%. When the degree of burn-off is between 50 and 75%, the product has a mixed porous structure and contains all types of pores.

Active carbons, in general, have a strongly developed internal surface and they are usually characterized by a polydisperse capillary structure comprising pores of different sizes and shapes. It is difficult to obtain accurate information on the shape of the pores. Several different methods used to determine the shapes of the pores have indicated ink-bottle shape, capillaries open at both ends or with one end closed, regular slit-shaped, V-shaped, and many other shapes.<sup>6,7</sup> It may, however, be mentioned that for all practical purposes, the actual shape of the pores is of no consequence. Generally, the calculations of the pore radii are made by considering the pores to be ink-bottle shaped or straight and nonintersecting cylindrical capillaries.

Active carbons are associated with pores starting from less than a nanometer to several thousand nanometers. Dubinin<sup>8</sup> proposed a classification of the pores that has now been adopted by the International Union of Pure and Applied Chemistry (IUPAC).<sup>9</sup> This classification is based on their width (w), which represents the distance between the walls of a slit-shaped pore or the radius of a cylindrical pore. The pores are divided into three groups: the micropores, the mesopores (transitional pores), and the macropores.

Micropores have molecular dimensions, the effective radii being less than 2 nm. The adsorption in these pores occurs through volume filling, and there is no capillary condensation taking place. The adsorption energy in these pores is much larger compared to larger mesopores or to the nonporous surface because of the overlapping of adsorption forces from the opposite walls of the micropores. They generally have a pore volume of 0.15 to 0.70 cm<sup>3</sup>/g. Their specific surface area constitutes about 95% of the total surface area of the active carbon. Dubinin<sup>10</sup> further suggested that for some active carbons, the microporous structure can be subdivided into two overlapping microporous structures involving specific micropores with effective pore radii smaller than 0.6 to 0.7 nm and the super micropores showing radii of 0.7 to 1.6 nm. The micropore structure of active carbons is characterized largely by the adsorption of gases and vapors and, to a smaller extent, by small-angle x-ray scattering technique.

Mesopores, also called *transitional pores*, have effective dimensions in the 2 to 50 nm range, and their volume usually varies between 0.1 and 0.2 cm<sup>3</sup>/g. The surface area of these pores does not exceed 5% of the total surface area of the carbon. However, by using special methods, it is possible to prepare activated carbons that have an enhanced mesoporosity, the volume of mesopores attaining a volume of 0.2 to 0.65 cm<sup>3</sup>/g and their surface area reaching as high as 200 m<sup>2</sup>/g. These pores are characterized by capillary condensation of the adsorbent with the formation of a meniscus of the liquefied adsorbate. The adsorption isotherms show adsorption desorption hysteresis is which stops at a relative vapor pressure of 0.4. Besides contributing significantly to the adsorption of the adsorbate, these pores are generally characterized by adsorption-desorption isotherms of gases, by mercury porosimetry, and by electron microscopy.

Macropores are not of considerable importance to the process of adsorption in active carbons because their contribution to the surface area of the adsorbate is very small and does not exceed  $0.5 \text{ m}^2/\text{g}$ . They have effective radii larger than 50 nm, and frequently in the 500 to 2000 nm range, with a pore volume between 0.2 and 0.4 cm<sup>3</sup>/g. They act as transport channels for the adsorbate into the micro- and mesopores. Macropores are not filled by capillary condensation and are characterized by mercury porosimetry.

Thus, the porous structure of active carbons is tridisperse, consisting of micro-, meso-, and macropores. Each of these groups of pores plays a specific role in the adsorption process. The micropores constitute a large surface area and micropore volume and, therefore, determine to a considerable extent the adsorption capacity of a given active carbon, provided that the molecular dimensions of the adsorbate are not too large to enter the micropores. Micropores are filled at low relative vapor pressure before the commencement of capillary condensation. The mesopores, on the other hand, are filled at high relative pressures with the occurrence of capillary condensation. The macropores enable adsorbate molecules to pass rapidly to smaller pores situated deeper within the particles of active carbons. Thus, according to Dubinin, the pattern of porous structure in active carbons constitutes macropores opening up directly to the external surface, the transitional pores branching off from the macropores, and the micropores in turn branching off from the transitional pores.

It is worthwhile to mention that Dubinin classification of pores in active carbons is not entirely arbitrary because it takes into account differences in the behavior of molecules adsorbed in micro- and mesopores. Although adsorption-desorption hysteresis is characteristic of mesopores, it has also been observed in the case of micropores at low relative pressures.<sup>11,12</sup> This has been attributed to inelastic distortion of some micropores, resulting in trapping of the adsorbate molecules. Consequently, the accessibility of the micropore system has been found to be increased after a number of adsorption-desorption cycles.<sup>13</sup>

All pores have walls and, therefore, will show two types of surfaces: the internal or microporous surface denoted by  $S_{mi}$  and the external surface,  $S_e$ . The former represents the walls of the pores and has an area of several hundred square meters per gram of the carbon. It is given by the relationship

$$S_{mi} = \frac{2 \times 10^3 W}{L}$$

where  $S_{mi}$  is the surface area in m<sup>2</sup>/g, W is the volume in cm<sup>3</sup>/g, and L is the accessible pore width in nanometers. Because the pore width L is very small, the area of the micropores is much larger than the area of mesopores or macropores. The second surface,  $S_e$ , which constitutes the walls of the meso- and macropores as well as the edges and the outer facing aromatic sheets, is small and varies between 10 and 200 m<sup>2</sup>/g for many of the active carbons. The difference between  $S_{mi}$  and  $S_e$  lies in the volume of the adsorption energy, which can be twice as high on the walls of a micropore as on the open surface.<sup>13,14</sup> This energetic effect decreases rapidly as the pore width increases. As the adsorption in micropores takes place at low relative pressures and as the BET approach is unable to interpret the early stages of the

adsorption isotherm at low relative vapor pressures, the surface areas of highly micropores carbons obtained using the BET equation are many times unrealistic.

#### 1.3 CHEMICAL STRUCTURE OF THE CARBON SURFACE

The crystalline structure of a carbon has a considerable influence on its chemical reactivity. However, the chemical reactivity at the basal plane sites is considerably lower than at the edge sites or at defect positions. Consequently, highly graphitized carbons with a homogenous surface consisting predominantly of basal planes are less reactive than amorphous carbons. Grisdale<sup>15</sup> and Hennig<sup>16</sup> observed that the oxidation rates of carbon atoms at the edge sites were 17 to 20 times greater than at the basal plane surface. Similarly, intercalation reactions that involve dimensional changes to the carbon structure are possible only with highly graphitized carbons because of their high degree of order.

Besides the crystalline and porous structure, an active carbon surface has a chemical structure as well. The adsorption capacity of active carbons is determined by their physical or porous structure but is strongly influenced by the chemical structure. The decisive component of adsorption forces on a highly ordered carbon surface is the dispersive component of the van der Walls forces. In graphites that have a highly ordered crystalline surface, the adsorption is determined mainly by the dispersion component due to London forces. In the case of active carbons, however, the disturbances in the elementary microcrystalline structure, due to the presence of imperfect or partially burnt graphitic layers in the crystallites, causes a variation in the arrangement of electron clouds in the carbon skeleton and results in the creation of unpaired electrons and incompletely saturated valences, and this influences the adsorption properties of active carbons, especially for polar and polarizable compounds.

Active carbons are almost invariably associated with appreciable amounts of oxygen and hydrogen. In addition, they may be associated with atoms of sulfur, nitrogen, and halogens. These heteroatoms are derived from the starting material and become a part of the chemical structure as a result of imperfect carbonization, or they become chemically bonded to the surface during activation or during subsequent treatments. There is also evidence that the carbon can adsorb certain molecular species such as amines, nitrobenzene, phenols, and several other cationic species.

X-ray diffraction studies have shown that these heteroatoms or molecular species are bonded to the edges and corners of the aromatic sheets or to carbon atoms at defect positions and give rise to carbon-oxygen, carbon-hydrogen, carbon-nitrogen, carbon-sulfur, and carbon-halogen surface compounds, also known as *surface groups* or *surface complexes*. These heteroatoms can also be incorporated within the carbon layers forming heterocyclic ring systems. Because these edges constitute the main adsorbing surface, the presence of these surface properties of active carbons.

#### 1.3.1 CARBON-OXYGEN SURFACE GROUPS

Carbon-oxygen surface groups are by far the most important surface groups that influence the surface characteristics such as wettability, polarity, and acidity, and physico-chemical properties such as catalytic, electrical, and chemical reactivity of these materials. In fact, the combined oxygen has often been found to be the source of the property by which a carbon becomes useful or effective in certain respects. For example, the oxygen has an important effect on the adsorption capacity of carbons for water and other polar gases and vapors, on their ageing during storage, on the adsorption of electrolytes, on the properties of graphite as well as on its properties as a moderator in nuclear reactors. In the case of carbon fibers, these surface groups determine their adhesion to plastic matrices and consequently their composite properties. According to Kipling,<sup>17</sup> the atoms of oxygen and hydrogen are essential components of an active carbon with good adsorptive properties, and the surface of such materials is to be considered as a hydrocarbon surface modified at some points by oxygen atoms.

Although the determination of the number and nature of these surface chemical groups began more than 50 years ago, the precise nature of the functional groups is not entirely established. The estimations obtained by different workers using varied techniques differ considerably because the carbon surface is very complex and difficult to reproduce. The surface groups cannot be treated as ordinary organic compounds because they interact differently in different environments. They behave as complex structures presenting numerous mesomeric forms, depending upon their location on the same polyaromatic frame. Recent electron spectroscopy for chemical analysis (ESCA) studies have shown that irreversible transformation of surface groups occurred when classical organic chemistry methods were used to identify and estimate them. It is Thus, expected that the application of more sophisticated techniques such as FTIR, XPS, NMR spectroscopy, and radiotracer studies will contribute significantly to a more precise knowledge about these surface chemical groups.

Carbons have great tendency to extend this layer of chemisorbed oxygen, and many of their reactions arise because of this tendency. For example, carbons are capable of decomposing oxidizing gases such as ozone<sup>18–21</sup> and oxides of nitrogen,<sup>22,23</sup> chemisorbing oxygen. They also decompose aqueous solutions of silver salts,<sup>24</sup> halogens,<sup>25–27</sup> ferric chloride,<sup>28</sup> potassium and ammonium persulphate,<sup>29–33</sup> sodium hypochlorite,<sup>34</sup> potassium permanganate,<sup>35,36</sup> potassium dichromate,<sup>35</sup> sodium thiosulphate,<sup>37</sup> hydrogen peroxide,<sup>38,39</sup> and nitric acid.<sup>31–33,40,41</sup> In each case, there is chemisorption of oxygen and the formation of carbon-oxygen surface compounds. Carbons can also be oxidized by heat treatment in air, CO<sub>2</sub>, or oxygen. The nature and amount of surface oxygen groups formed by different oxidative treatments depend upon the nature of the carbon surface and the history of its formation, its surface area, the nature of the oxidative treatment, and its temperature.

The reaction of activated carbons with oxygen gas at temperatures below 400°C predominantly results in the chemisorptions of oxygen and the formation of carbon-oxygen surface compounds, whereas at temperatures above 400°C the

decomposition of the surface compounds and the gasification of the carbon are the predominating reactions.

$$\begin{array}{ll} C+O_2 \xrightarrow{<400^{\circ}C} C(O) & \text{Formation of surface compound.} \\ C+O_2 \xrightarrow{>400^{\circ}C} CO+CO_2 & \text{gasification} \\ C(O) \xrightarrow{>400^{\circ}C} CO+CO_2 & \text{decomposition of surface compound.} \end{array}$$

In the case of oxidations in the solution phase, the major reaction is the formation of the surface compound, although some gasification may also take place depending upon the strength of the oxidative treatment and the severity of the experimental conditions. The formation of carbon-oxygen surface compounds using different active carbons and carbon black, and using various oxidative treatment in gaseous and solution phase, has been studied by a large number of investigators and has been very well reviewed.<sup>1,41–45</sup> Thus, we merely point out that carbons have a tendency to pick upon oxygen, at least to some extent under all conditions.

Carbons have an acid-base character. This fact has encouraged many investigators to devote their research effort to understand the cause and mechanism by which a carbon acquires an acid or a base character. Several theories (e.g., the electrochemical theory of Burstein and Frumkin,<sup>46,47</sup> the oxide theory of Shilov and his school,<sup>48</sup> the chromene theory of Garten and Weiss,<sup>43,49</sup> and the pyrone theory of Voll and Boehm,<sup>50</sup> have been proposed to explain the acid-base character of carbons. These theories and the related work have been elaborately reviewed and critically examined in several review articles.<sup>42-44</sup> It is now well accepted that the acid-base character of carbons is developed as a result of surface oxidation and depends on the history of formation and the temperature of oxidation.

Three types of carbon-oxygen surface groups (acidic, basic, and neutral) have been recognized. The acidic surface groups are very well characterized and are formed when carbon is treated with oxygen at temperatures up to 400°C or by reaction with oxidizing solutions at room temperature. These surface groups are thermally less stable and decompose on heat treatment in vacuum or in an inert atmosphere in the temperature range of 350 to 750°C evolving  $CO_2$ . These acidic surface groups render the carbon surface hydrophilic and polar in character and have been postulated to be carboxylic, lactone, and phenolic groups.

The basic surface oxygen groups are much less characterized and are obtained when a carbon surface, freed of all surface oxygen groups by heat treatment in vacuum or in inert atmosphere at 1000°C, and after cooling to room temperature, is contacted with oxygen gas. Garten and Weiss<sup>43,49</sup> proposed a pyrone-type structure for basic surface groups, which has also been referred to as a *chromene structure*. This structure has a heterocyclic oxygen-containing ring with an activated = CH<sub>2</sub> or = CHR (*R* is an alkyl group) group. According to Voll and Boehm,<sup>50</sup> the oxygen atoms in the pyrone-like structure are located in two different rings of a graphitic layer. Out of the two differently bonded oxygen atoms on the basic surface sites, one decomposes into CO<sub>2</sub> and CO at 900°C and the other at 1200°C (Figure 1.3).

However, the structure of the basic surface oxygen groups is still a matter of dispute. Morterra et al.<sup>51</sup> are emphatic that the basic properties of carbons cannot



**FIGURE 1.3** Functional groups of basic character: (a) chromene (After Garten, V.A. and Weiss, D.E., *Rev. Pure Appl. Chem.*, 7, 69, 1957. With permission.), (b) pyrone-like. (After Boehm, H.P., in *Advances in Catalysis*, Vol. XVI, Academic Press, New York, 1966, p. 179. With permission.)

be assigned to well-defined oxygen structures confirming the earlier view of Puri<sup>44</sup> that the basic character of carbons cannot be attributed to the existence of chromene or any other oxygen-containing surface groups. It appears that there is need for further work before the existence or the structure of basic groups can be accepted.

The neutral surface oxygen groups are formed by the irreversible chemisorption of oxygen at the ethylene type unsaturated sites present on the carbon surface.<sup>44</sup>

The surface compound decomposes into  $CO_2$  on heat treatment. The neutral surface groups are more stable than the acidic surface groups and start decomposing in the temperature range 500 to 600°C and are removed completely only at 950°C. A model of the fragment of an oxidized active carbon surface proposed by Tarkovskya<sup>52</sup> is shown in Figure 1.4.

#### 1.3.2 CHARACTERIZATION OF CARBON-OXYGEN SURFACE GROUPS

A considerable amount of effort has been directed to identify and estimate carbonoxygen surface groups (or functional groups) using several physical, chemical, and physicochemical techniques that include desorption of the oxide layer, neutralization with alkalies, potentiometric, thermometric, and radiometric titrations, and spectroscopic methods such as IR spectroscopy and x-ray photoelectron spectroscopy. These studies have shown the existence of several groups, the more important being the carboxyls, lactones, phenols, quinones, and hydroquinones. However, these methods have not yielded comparable results and many times the entire amount of the associated oxygen has not been accounted for. Puri<sup>44</sup> suggested caution in the interpretation of



FIGURE 1.4 Model of a fragment of an oxidized active carbon surface. (After Tarkovskya, I.A., Strazhesko, D.N., and Goba, W.E., Adsorbtsiya, *Adsorbenty*, 5, 3, 1977. With permission.)

the results because the surface groups on carbons are unlikely to behave exactly in the same way as those in simple organic compounds. Thus, a brief discussion of the results obtained by these methods in the identification and estimation of the surface oxygen group present on different carbons is appropriate in this chapter.

#### 1.3.2.1 Thermal Desorption Studies

The surface oxygen groups found on as-received carbons, or formed as a result of interaction with oxygen or with oxidizing gases or solutions, have different thermal stabilities because they are formed at different sites associated with varying energies. For example, carboxyl groups decompose at lower temperatures than phenolic or quinone groups. Thus, when a carbon sample is heat treated in vacuum or in an inert atmosphere, different surface groups decompose in different temperature ranges. In general, it has been observed that these surface groups are thermally stable at temperatures below 200°C, independent of the temperature at which they are formed.

The technique generally involves heating the carbon sample in vacuum or in an inert flowing carrier gas at a programmed heating rate. The oxygen-containing surface groups decompose into volatile gaseous products, which are then analyzed by conventional methods such as gravimetry, mass spectroscopy, gas chromatography, and IR spectroscopy. Because carbon is highly reactive with oxygen, the carbon-oxygen surface groups are generally evolved as  $CO_2$ , CO, and water vapor, the amount of each gaseous species depending upon the nature of the carbon, its pretreatment, and the thermal desorption temperature. For example, CO<sub>2</sub> is evolved by the decomposition of carboxylic and lactomic groups in the temperature range 350 to 750°C; CO by the decomposition of quinone and phenolic groups in the temperature range 500 to 950°C; water vapor from the decomposition of carboxyls, phenols in the temperature range 200 to 600°C. At lower temperatures some physisorbed and chemisorbed water is also desorbed. Some elementary hydrogen gas formed by the recombination of evolved hydrogen atoms as a result of splitting of C-H bonds is desorbed in the temperature range 500 to 1000°C. It may be pointed out that about 25 to 30% of the elementary hydrogen remains bonded to the interior of the carbon atoms, even after degassing at 1000°C.

Numerous studies on the thermal desorption of different carbons have been reported. Puri and Bansal<sup>53</sup> and Bansal et al.<sup>54</sup> carried out vacuum pyrolysis of a number of carbon blacks, charcoals, and activated carbons, and measured the amount of oxygen evolved as  $CO_2$ , CO, and water vapor as a function of heat treatment temperature. The total of the three oxygens (evolved as  $CO_2$ , CO, and water vapor) agreed fairly with the total oxygen obtained by ultimate analysis (Table 1.1 to Table 1.3). The desorption of oxygen as  $CO_2$  and CO on evacuation at gradually increasing temperatures (Figure 1.5 and Figure 1.6) shows that these gases are evolved in different temperature ranges, which indicates that the chemisorbed oxygen constitutes different surface groups that involve different sites associated with varying energies. The composition of the evolved gas in a particular temperature range appears to depend upon the nature of the surface group or groups decomposing in that range.

Bansal et al.<sup>55</sup> also studied the decomposition of carbon-oxygen surface groups formed on low temperature oxidation of ultra clean surfaces of activated graphon using a mass spectrometer and observed that both CO<sub>2</sub> and CO were primary

Sample		O <sub>2</sub> Evol Outgassing (g/10	ved on at 1200°C 0 g)		Oxygen by Ultimate Analvsis	Hydrogen I at 1:	Evolved on ( 200°C (g/1(	Outgassing )0 g)	Hydrogen by UltimateAnalysis (g/100 g)
Identification	$CO_2$	CO	$H_2O$	Total	(g/100 g)	$H_2O$	H <sub>2</sub>	Total	) )
PF-140°	7.00	13.05	2.05	22.10	22.80	0.26	3.60	3.86	4.90
$PF-400^{\circ}$	4.90	5.10	1.30	11.30	10.40	0.16	2.85	3.01	4.20
$PF-600^{\circ}$	1.40	4.60	Tr	6.00	3.90	Tr	2.00	2.00	2.90
$PF-900^{\circ}$	0.50	1.60	Tr	2.10	1.40	Tr	1.05	1.05	1.30
PVDC-600°	3.50	2.00	0.20	5.70	3.60	0.03	1.49	1.52	0.80
PVC-850° (vac)	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr
$PVC-850^{\circ}(N_2)$	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr
PVC-850° (CO <sub>2</sub> )	1.01	0.48	0.18	1.67	1.81	0.02	0.30	0.32	0.65
$UF-400^{\circ}$	2.80	4.80	2.40	10.00	10.62	0.30	2.95	3.25	4.27
UF-650°	2.59	4.08	Tr	6.67	6.05	Tr	2.25	2.25	3.50
UF-850°	0.25	1.71	Tr	1.96	2.10	Tr	0.30	0.30	0.50

TABLE 1.1 Gases Evolved on Outgassing Various Polymer Carbons at 1200°C

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Source: Bansal, R.C., Dhami, T.L., and Prakash, S., Carbon, 15, 157, 1977. Reproduced with permission from Elsevier.

		Nitrogen Surface	Oxyg	en Evolved at 1200°C,	l on Outga (g/100 g)	ssing	Oxygen by Ultimate Analysis,	Hydro Outga	gen Evolve ssing at 12 (g/100 g)	ed on 00°C,	Hydrogen by Ultimate Analysis
Trade Name	Type	Area (m <sup>2</sup> /g)	CO <sub>2</sub>	CO	H <sub>2</sub> O	Total	%	$H_2O$	$H_2$	Total	%
Pelletex	Furnace	27.1	0.051	0.331	0.133	0.52	0.22	0.016	0.238	0.25	0.38
Kosmos-40	Furnace	31.2	0.088	0.320	0.017	0.48	0.23	0.009	0.209	0.22	0.35
Statex-B	Furnace	48.3	0.115	0.400	0.089	0.60	0.43	0.011	0.248	0.26	0.36
Philblack-A	Furnace	45.8	0.187	0.343	0.000	0.53	0.58	0.000	0.209	0.21	0.35
Philblack-O	Furnace	79.6	0.209	0.428	0.107	0.74	0.79	0.013	0.207	0.22	0.30
Philblack-I	Furnace	116.8	0.348	0.628	0.355	1.33	1.17	0.042	0.139	0.18	0.29
Philblack-E	Furnace	135.1	0.401	0.411	0.435	1.26	1.01	0.054	0.137	0.19	0.31
Vulcan-SC	Channel	194.4	0.428	0.800	0.133	1.36	1.18	0.016	0.094	0.11	0.17
Spheron-9	Channel	115.8	0.536	1.928	0.710	3.17	3.49	0.089	0.321	0.41	0.62
Spheron-6	Channel	120.0	0.500	2.122	0.462	3.08	3.10	0.058	0.284	0.34	0.55
Spheron-4	Channel	152.7	0.547	2.829	0.689	4.06	3.28	0.086	0.232	0.32	0.47
Spheron-C	Channel	253.7	0.575	2.000	0.600	3.17	3.14	0.075	0.152	0.23	0.33
ELF-O	Color	171.0	1.176	2.171	0.710	4.05	4.89	0.089	0.247	0.34	0.47
Mogul-A	Color	228.4	1.894	4.228	0.979	7.10	7.63	0.122	0.236	0.36	0.51
Mogul	Color	308.0	2.205	4.180	1.440	7.82	8.22	0.180	0.132	0.31	0.48

Activated Carbon and Its Surface Structure

TABLE 1.2

Gases Evolved or	n Evacuating	g Mogul and	Mogul-A at I	<b>Different</b> Ten	nperatures		
	X	eight Percent O	vygen Evolved A	S:	Weight Perce	nt Hydrogen Ev	olved As:
Temperature,°C	CO <sub>2</sub>	CO	H <sub>2</sub> O	Total	H <sub>2</sub> O	H	Total
			Mogul				
30-200							
200-300	0.220		0.178	0.398	0.022		0.022
300-400	0.661		0.417	1.078	0.052		0.052
400-500	0.655		0.791	1.446	0.099		0.099
500-700	0.371	1.314	0.009	1.694	0.001	0.030	0.031
700-800	0.269	2.000	0.019	2.288	0.002	0.085	0.087
800-1000	0.008	0.612	0.026	0.646	0.003	0.082	0.085
1000-1200	0.014	0.251	0.009	0.274	0.001	0.007	0.008
			Mogul-A				
30-200		I			Ι		
200-300	0.356	I	0.196	0.552	0.024		0.024
300-400	0.579		0.160	0.739	0.020		0.020
400-500	0.519		0.533	1.052	0.067		0.067
500-700	0.417	1.071	0.044	0.532	0.005	0.035	0.040
700-800	0.004	0.739	0.045	1.788	0.006	0.092	0.098
800-1000	0.010	0.830	0.000	0.840	0.000	0.084	0.084
1000-1200	0.000	0.590		0.590		0.025	0.025
Source: Puri, B.R. and	l Bansal, R.C., 0	Carbon, 1, 451, 19	964. Reproduced	with permission	from Elsevier.		

 TABLE 1.3
 Gases Evolved on Evacuating Mogul and Mogul-A at Different Temperatur

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**FIGURE 1.5** Oxygen evolved as CO<sub>2</sub> on outgassing polymer charcoals at different temperatures. (After Bansal, R.C., Dhami, T.L., and Prakash, S., *Carbon*, 15, 157, 1977. With permission.)

products obtained by the decomposition of different oxygen functional groups from different sites on the carbon surface.

The nature of the gaseous species evolved on thermal desorption of carbonoxygen surface groups and the mechanism of their evolution was also studied by Van Driel<sup>56</sup> using gas chromatography, by Lang and Magnier<sup>57</sup> using IR and gas chromatography, by Bonnetain et al.<sup>58,59</sup> using chemical separation techniques, by Tucker and Mulcahy<sup>60</sup> using thermogravimetric technique, and by Dollimore et al.<sup>61</sup> using mass spectrometry. These workers observed that the major part of the surface



**FIGURE 1.6** Oxygen evolved as CO on outgassing polymer charcoals at different temperatures. (From Bansal, R.C., Dhami, T.L., and Prakash, S., *Carbon*, 15, 157, 1977. With permission.)



**FIGURE 1.7** Desorption of chemisorbed oxygen from oxidized diamond (D) and graphite (G) as a function of temperature. (From Matsumoto, S. and Setaka, N., *Carbon*, 17, 303, 1979. With permission.)

groups decomposed in the temperature range 600 to 800°C and almost completely at 1000°C. The amount of oxygen evolved could be almost completely accounted for by the evolution of  $CO_2$  and CO. The activation energy for desorption was found to increase with decreasing surface coverage, indicating that the evolution of different gases involved the decomposition of different surface species.

Trembley et al.<sup>62</sup> measured desorption energies of carbon oxygen surface groups on graphon, using linear programmed thermal desorption, and observed that the desorption energies were a function of the surface coverage, indicating that the surface oxygen complex consisted of several types of surface functional groups that decomposed in different temperature ranges. Matsumoto and Setaka<sup>63</sup> carried out thermal desorption studies of oxidized vitreous carbon, diamond, and graphite at temperatures up to 950°C using a mass spectrometer. The desorption spectra (Figure 1.7) of the samples showed two different maxima for CO<sub>2</sub> and CO as a function of temperature, indicating once again that the gases are being desorbed by the decomposition of different surface compounds.

Thus, there is overwhelming evidence from thermal desorption studies that there are two types of surface chemical structures that involve different sites associated with varying energies, and that  $CO_2$  and CO are evolved by the decomposition of these two types of surface groups. The surface groups that evolve  $CO_2$  are less stable and decompose at temperatures as low as 350°C. The other chemical groups that evolve CO are more stable and decompose only above 500°C. The interpretation of the results is generally difficult because the surface groups behave differently in different environments. They can interact directly with similar or other groups in the neighborhood. In general, the thermal desorption studies yield valuable information that supplements the results obtained by other independent methods.

#### 1.3.2.2 Neutralization of Alkalies

Titration with alkalies is one of the earliest and simplest methods used to determine the nature and amount of surface acidic groups on carbons. However, the standard conditions under which comparable results can be obtained have been realized during the last few decades. It is now recognized that the base neutralization capacity of a carbon should be determined after degassing the sample at ~150°C so as to free it from any physically adsorbed gases and vapors. The carbon sample is then placed in contact with a 0.1 to 0.2 N alkali solution for 24 to 72 hr. The contact time can be reduced to a few hours if the carbon and the alkali solution are heated under reflux. These conditions are now being followed by many of the investigators.

Puri and coworkers<sup>64</sup> examined a large number of charcoals before and after outgassing, and extensive oxidation treatments in oxygen as well as in oxidizing solutions, and tried to correlate the base neutralization capacity of the charcoal with the oxygen evolved as  $CO_2$  on evacuation. It was found (Table 1.4) that in each case the amount of alkali neutralized was close to the amount of CO<sub>2</sub> evolved on evacuation (termed CO<sub>2</sub> complex). As the amount of the CO<sub>2</sub> complex decreased on outgassing or increased on oxidation, the base neutralization capacity of the charcoal decreased or increased correspondingly. When the entire amount of the complex was removed on outgassing around 750°C, the carbon lost almost completely its capacity to neutralize alkalies, even though it still contained appreciable amounts of associated oxygen (cf. Table 1.4). This work was later extended to commercial-grade carbon blacks by Puri and Bansal.<sup>66</sup> Their surface acidity, as determined by neutralization of sodium and barium hydroxides, was found to be close to each other as well as to the amount of CO<sub>2</sub> complex contained in each sample. Puri and Mahajan,<sup>67</sup> Anderson and Emmett,<sup>68</sup> and Puri et al.<sup>69</sup> studied the adsorption of ammonia and several amines on several charcoals and carbon blacks and found that the amount adsorbed was close to the amount of  $CO_2$  complex present on the carbon surface.

Thus, Puri and coworkers are of the view that in charcoals as well as in carbon blacks, the same surface group that is involved in the liberation of  $CO_2$  on evacuation is also involved in the neutralization of alkalies. This cannot be a carboxylic group because there is no significant correlation between  $CO_2$  evolved and active hydrogen. This cannot be a lactone group as suggested by Garten and Weiss<sup>43</sup> because it did not show equivalence between  $CO_2$  evolved and alkali neutralized. However, these workers did not rule out the possibility of the existence of certain types of lactone structure that would hydrolyze to give a carboxylic group and a phenolic group, each capable of stoichiometric ionic adsorption.

Boehm<sup>42</sup> differentiated the acidic surface groups on oxidized charcoal and carbon black by selective neutralization technique, using bases of different strengths, namely NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaOH, and C<sub>2</sub>H<sub>5</sub>ONa (Table 1.5). The strongly acidic groups neutralized by NaHCO<sub>3</sub> but not by Na<sub>2</sub>CO<sub>3</sub> were postulated as lactones. The weakly acidic group neutralized by NaOH but not by Na<sub>2</sub>CO<sub>3</sub> was postulated as a group of phenols. The reaction with sodium ethoxide was not considered a true neutralization reaction because it did not involve an exchange of H<sup>+</sup> ions by Na<sup>+</sup> ions. The groups reacting with sodium ethoxide but not with sodium hydroxide were suggested to be carboxyls, which were created by the

#### **TABLE 1.4**

## Relationship Between Base Neutralization Capacity and $CO_2$ Evolved on Evacuation of Various Charcoals at 1200°C

Carbon Sample	CO <sub>2</sub> Evolved On Evacuation At 1200°C (meq/100 g)	Sodium Hydroxide Neutralized (meq/100 g)	Barium Hydroxide Neutralized (meq/100 g)
Sugar charcoal			
Original	669	662	664
300°-outgassed	388	381	377
400°-outgassed	231	222	228
500°-outgassed	150	153	147
600°-outgassed	75	74	72
750°-outgassed	0	0	0
1000°-outgassed	0	0	0
Oxidized with H <sub>2</sub> O <sub>2</sub>	819	810	815
Oxidized with K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	975	970	965
Coconut charcoal			
Original	394	395	400
300°-outgassed	181	165	170
500°-outgassed	38	35	20
600°-outgassed	15	12	16
750°-outgassed	0	0	0
1000°-outgassed	0	0	0
Oxidized with H <sub>2</sub> O <sub>2</sub>	591	584	582
Oxidized with K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	623	627	619
Wood charcoal			
Original	531	532	535
300°-outgassed	400	399	405
500°-outgassed	50	50	49
600°-outgassed	22	17	25
750°-outgassed	0	0	0
1000°-outgassed	0	0	0
Cotton stalk charcoal			
Original	325	335	342
300°-outgassed	250	245	251
500°-outgassed	62	65	63
600°-outgassed	15	21	16
750°-outgassed	0	0	0
1000°-outgassed	0	0	0

Source: Puri, B.R., Singh, D.D., Nath, J., and Sharma, L.R., Ind. Engg. Chem., 50, 1071, 1958. With permission.

## TABLE 1.5Selective Neutralization of Acidic Surface Structureson Microcrystalline Carbons

		Neutralizatior	ı (meq/g) by	
Carbon Sample	Sodium Bicarbonate	Sodium Carbonate	Sodium Hydroxide	Sodium Ethoxide
Sugar charcoal heat-treated in nitrogen at 1200°C	0.16	0.32	0.69	0.85
Sugar charcoal (activated)	0.21	0.43	0.72	0.89
Sugar charcoal activated and	0.35	0.73	1.02	1.38
then heat-treated				
Eponite	0.16	0.34	0.63	1.06
CK-3	0.76	1.52	2.37	3.15
Philblack-O	0.57	1.09	1.64	2.34
Spheron-6	0.59	1.18	1.96	2.95
Spheron-C	0.64	1.28	1.88	2.56
Sugar charcoal oxidized with KMnO <sub>4</sub>	0.39	0.64	0.88	0.96
Eponite oxidized with KMnO <sub>4</sub>	0.78	1.15	1.61	2.21
Eponite oxidized with $(NH_4)_2S_2O_8$	0.88	1.34	1.74	2.35
Eponite oxidized with NaOCl	1.08	1.64	2.15	2.61
CK-3 oxidized with $(NH_4)_2S_2O_8$	0.20	0.31	0.35	0.58

*Source*: Boehm, H.P., in *Advances in Catalysis*, Vol. XVI, Academic Press, New York, 1966, p. 179. With permission.

oxidation of the disorganized aliphatic carbon. Puri,<sup>44</sup> however, questioned the validity of the selective neutralization technique.

According to Puri, the same acid group will neutralize different amounts of alkalies of varying strengths. For example, a weak acid-like acetic acid can be neutralized only partially when titrated against Na<sub>2</sub>CO<sub>3</sub> or NaHCO<sub>3</sub>, but the same acid can be neutralized completely by NaOH. Barton et al.<sup>70–73</sup> while studying the surface oxygen structures on a sample of graphite and a carbon black by degassing at different temperatures, using a mass spectrometer and by measuring base neutralization capacities of the degassed samples, suggested that the acidic group present on the surface of graphite was monobasic and that the carbon black contained both a monobasic and a dibasic surface acidic group. Combining these studies with reaction with methyl magnesium iodide<sup>70</sup> and diazomethane,<sup>71</sup> these workers suggested that both the groups on carbon black were lactones, but only one of them had active hydrogen associated with it.

Bansal et al.<sup>74</sup> combined desorption and base neutralization techniques for investigating the acidic surface groups on several polymer carbons. The base neutralization capacity using sodium hydroxide was found to be almost exactly equivalent to the amount of  $CO_2$  evolved on evacuation in the case of polyvinylidene (PVDC), polyvinyl chloride

TABLE	1.6				
Alkalis	Neutralized	by Various	Polymer	Carbons in	Relation
to CO <sub>2</sub>	Evolved on	<b>Evacuation</b>			

Sample	Sodium Hydroxide Neutralized (meq/100 g)	CO <sub>2</sub> Evolved on Evacuation (meq/100 g)	Sodium Ethoxide Neutralized (meq/100 g)
PVDC-600°	212	218	256
PVDC-850° (CO <sub>2</sub> )	62	63	71
Saran-600°	150	146	171
PF-600°	42	87	56
PF-900°	16	31	21
UF-650°	78	162	109
UF-850°	7	16	11

Source: Bansal, R.C., Bhatia, N., and Dhami, T.L., Carbon, 16, 65, 1978. Reproduced with permission from Elsevier.

(PVC), and Saran (a copolymer of PVDC and PVC) charcoals but was almost half of the amount of  $CO_2$  evolved in the case of polyfurfurylalocbol (PF) and urea formoledeloyde (UF) charcoals (Table 1.6). The base neutralization capacity decreased on evacuation, and the decrease at any temperature corresponded to the amount of  $CO_2$  evolved at that temperature. Furthermore, the temperature interval over which the drop in base neutralization occurred appears to be the same (Figure 1.8) as the temperature interval over which  $CO_2$  was evolved from the carbon sample.



**FIGURE 1.8** Base adsorption capacity in relation to evacuation temperature. (From Bansal, R.C., Bhatia, N., and Dhami, T.L., *Carbon*, 16, 65, 1978. With permission.)

The possible structure for a lactone that could explain most of the data obtained by them and by others could be an f-lactone first suggested by Garten and Weiss<sup>43</sup> and later restated by Barton et al.<sup>70</sup> Bansal et al.<sup>74</sup> suggested that the lactone exists in two tautomeric forms. The keto form explains the results obtained for monobasic carbons, and the enol form fits well with the dibasic carbons such as PVDC, PVC, and Saran. The existence of these two forms in different carbons is quite reasonable, because the presence of individual oxygen surface groups and their proportions are very much dependent on the history of their preparation.

The base neutralization technique to measure surface acidic groups, although simple, requires a large sample size. Consequently, several workers<sup>66,75–81</sup> carried out electrometric measurements (potentiometric titrations) using a very small sample size because these measurements are very sensitive and accurate. The procedure essentially consists of preparing a suspension of the carbon in  $CO_2$ -free distilled water, adding a standard alkali solution in small amounts, and measuring the current using a precision instrument. The analysis of the shape of the titration curve and the inflection points determine the contribution of functional groups of different acidic strength to the surface acidity of the carbons.

#### 1.3.2.3 Specific Chemical Reactions

Several workers have used more direct analysis of the surface oxygen groups by studying specific chemical reactions of organic chemistry. Most of these reactions have been carried out in conjunction with other methods. The most important surface groups for which chemical analysis has been used are carboxyls, phenols, quinones and lactones. The more commonly used organic chemistry reaction is methylation of the carbon with diazomethane followed by hydrolysis of the methylated product with a mineral acid. The fraction that is hydrolyzed has been attributed to carboxylic groups<sup>82</sup> and to lactones.<sup>43</sup> The unhydrolyzable portion of the methylated product is considered to be due to phenolic groups. The quinone groups have generally been determined by reduction with sodium borohydride. The results of some of these studies on charcoals, carbon blacks, and activated carbons are presented in Table 1.7 and Table 1.8. The readers are directed to consult our earlier books on active carbon<sup>1</sup> and carbon black<sup>83</sup> for more detailed studies.

Surface group estimations using direct chemical analysis have not been able to account for the entire amount of associated oxygen. Thus, several workers have suggested caution in using these methods. Papirer and Guyon,<sup>80</sup> for example, on the basis of their surface group determination using organic methods and spectroscopic analysis, observed that the surface groups on carbons cannot be considered classical organic functional groups, but rather combined structures that may present numerous mesmeric forms largely favored by their locations on the same polyaromatic frame.

#### 1.3.2.4 Spectroscopic Methods

Several spectroscopic techniques have been used to investigate the presence of carbonoxygen surface groups on carbons. Infrared (IR) and electron spin resonance (ESR) are the two most commonly used spectroscopic techniques, although in more recent years, x-ray photoelectron spectroscopy (XPS) has been increasingly applied for the

			-OCH <sub>3</sub> Introdu	rced	Sodium Hydroxide Neutralized
	Sodium Hydroxide Neutralization		Hydrolyzable = COOH or Lactone Groups	Nonhydrolyzable = Phenolic Groups	Minus Total -OCH <sub>3</sub> n-lactone Groups
Carbon Sample	Capacity (meq/100 g)	Total	(meq/100 g)	(mEq/100 g)	(meq/100 g)
Sugar charcoal	81	82	50	32	I
Sugar charcoal heat-treated in nitrogen	69	72	34	38	I
Sugar charcoal activated in 202	71	72	42	30	
Eponite Sucar charcoal heated in air at	62	107	46	61	
tugu cuacoa neaca m an a	59	11	05	05	48
500°	14	2	1	1	12
300°	13	8	9	9	5
Sugar charcoal oxidized in					
air after evacuation at $800^{\circ}$					
400°	32	15	10	5	17
500°	22	15	11	4	17

TABLE 1.7 Surface Group Analysis by Reaction with Diazomethane

200∘	18	15	12	3	3
Carbolac-1	183	146	06	56	37
Mogul-A	118	54	33	21	64
ELF-O	58	24	14	10	34
Spheron-6	37	14	6	9	23
Spheron-9	46	10	5	5	36
<i>Sources</i> : Bansal, R.C., Bhatia, N., and Dh. <i>Ind. Engg. Chem.</i> , 48, 162, 1956; and Stu	ami, T.L., <i>Carbon</i> , 16 debaker, M.L. and Ri	5, 65, 1978; Studeba inehart, R.W., <i>Rubb</i>	ker, M.L., Huffman, E.W er Chem. Technol., 45, 1	V.D., Wolfe, A.C., and Na 06, 1972. With permissic	abors, L.G., on.

Carbon Sample	Oxygen as Phenol Group by Grignard Reagent (%)	Oxygen as Phenol Group by Neutralization of Barium Hydroxide (%)	Oxygen as Quinone Group by Reduction With Sodium Borohydride (%)	Oxygen Ether Group by Difference (%)
Pelletex	0.02	0.08	0.16	0.35
Stirling-V	0.03	0.07	0.22	0.23
Kosmos-40	0.08	0.14	0.15	0
Statex-B	0.06	0.17	0.16	0.44
Philblack-A	0.08	0.16	0.24	0.24
Philblack-O	0.11	0.14	0.41	1.16
Philblack-E	0.19	0.33	0.66	1.15
Spheron-9	0.20	0.60	0.92	2.63
Spheron-6	0.18	0.45	0.67	1.82
Spheron-C	0.39	0.76	0.89	1.31
ELF	0.54	0.78	1.10	2.34
Mogul-A	0.52	1.98	1.71	2.84
Mogul	0.71	2.52	2.03	3.18
Carbolac-2	0.96	4.25	2.62	1.84

### TABLE 1.8Surface Group Analysis by Specific Organic Reactions

Source: Studebaker, M.L. and Rinehart, R.W., Rubber Chem. Technol., 45, 106, 1972. With permission.

examination of carbon surface structures. Although a detailed description of the instruments and procedures used in these spectroscopic techniques is beyond the scope of this chapter, the discussion will focus on results obtained on carbons by various spectroscopic techniques listed in Table 1.9.

#### TABLE 1.9 Spectroscopic Techniques used in Surface Group Analysis of Carbon Materials

Reference
84,92,93
96,97,93
95,96
85,86,96
51,89–91,95,96
98-106

#### Infrared Spectroscopy

Infrared spectroscopy (IR) in its various forms is an important and forceful tool that can provide useful information about surface functional groups on carbons. Special IR studies can also provide information regarding the molecular forces involved in the adsorption processes. Carbon is black in color and so has a tendency to absorb most of the radiation, at least in the visible region. Even its thin sections are opaque. But it can transmit some radiations in the IR region when examined using thin sections. The developments leading to the preparation of halide pellets, in which finely divided carbonaceous samples were uniformly distributed, has made possible the application of IR to the study of carbon surfaces. Carbon blacks present no difficulties because they can be obtained in a very fine state of subdivision. Active carbons are hard and difficult to grind. However, this problem was solved by Friedel and Hofer,<sup>84</sup> who devised a technique by which active carbons and charcoals could be converted into a finely divided state for making halide pellets for IR studies.

The other difficulty in the IR studies of carbons using halide pellets is the exposure of the carbon material to atmospheric gases and vapors that tend to vitriate the results. The development of elaborate techniques for obtaining carbonaceous films and preparation of charcoals by carbonization under vacuum conditions<sup>51</sup> broadened the scope of applications of IR spectroscopy to the study of carbons and their surface groups. Furthermore, the sensitivity of IR measurements has been largely enhanced by using Fourier-Transform (FT), Photoacoustic (PAS), and Photothermal Beam Deflection (PDS) IR spectroscopy.

#### Transmission and Absorption Infrared Spectroscopy

In IR transmission and absorption (IR-T/A) studies, small amounts of carbon are mixed with KBr or Nujol. The typical composition of the carbon in the KBr pellet ranges from 0.01 to 0.5 weight percent and approximately 0.2 mg carbon/cm<sup>2</sup> of the pellet area. The carbon-Nujol mixture is made into a paste, which is spread into thin layers (less than 0.4 mm thick) for these measurements. As the carbon materials show strong absorption of radiations in the IR region, the spectra show low IR signal-to-noise ratio (s/n) for carbons. Thus, investigators are now turning to alternative and more sensitive techniques to enhance the signal and precision of the measurements.

#### Attenuated Total Reflectance IR Spectroscopy

In attenuated total reflectance IR spectroscopy (ATR-IRS), the spectra on the sample surface are measured by placing the carbon surface in close contact with a suitable reflecting element. Thus, there is restriction on the thickness of the carbon sample, because it involves measurement of the IR signal, which is reflected from the carbon surface and not the transmitted signal. The reflecting element used in such investigations is generally a trapezoidal prism, and the sample is placed on one or both of the reflecting surfaces. The beam generally enters at a right angle to one of the end faces and is reflected about 25 times before passing out of the reflecting surface determine the penetration of the IR beam into the sample surface. The reflecting element. The differences in the refractive indices of the sample surface. The reflecting elements most commonly used are the single crystals of AgCl, TiBr, and Ge, which have refractive indices of 2.0, 2.4, and 4.0, respectively. This technique has been successfully used in the case of carbon blacks.