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THERMOCHEMISTRY AND KINETICS OF OXYGEN INTERACTION WITH
MICROPOROUS CHARs

Technical Report 12

By
Ismail M. K. Ismail
Philip L. Walker

MASTER

January 1979
Date Published

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The Pennsylvania State University
Coal Research Section
University Park, Pennsylvania

U. S. DEPARTMENT OF ENERGY

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COAL RESEARCH SECTION
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ABSTRACT

In processes involving the hydrogasification of coal, the coal is first exposed to hydrogen at elevated temperatures and pressures during which devolatilization and gasification of the more reactive parts of the coal occur. A microporous coal char, which is relatively unreactive, is also produced. The char, in turn, can be reacted with steam to generate the hydrogen needed in the first part of the process. Or the char, in part, can be used in a boiler to raise steam. In any case, characterization of coal chars and the relation of character to behavior during gasification and/or combustion is important.

This report is primarily concerned with laying the experimental base for the measurement of the heat of interaction of a gas (oxygen in this case) with chars. Following the laying of this base, using a char produced from a reproducible polymer system, heats of interaction of oxygen with chars produced from American coals, ranging in rank from anthracite to lignite, were measured.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to study the exothermicity and kinetics of interaction between Saran chars and oxygen at selected isothermal temperatures in the range 75-850°C. A DuPont DSC cell was used in conjunction with a cell-base Module-II and a 990 Thermal Analyzer. A home-made TGA apparatus was constructed to meet the experimental demands.

Three major Saran chars, particle size (150 x 250 mesh), were used. The samples were characterized by determining: (i) active

surface areas (ASA), (ii) total surface areas, and (iii) mercury densities.

Prior to making measurements, each sample was outgassed at room temperature, flushed with ultrahigh purity nitrogen, heated at 20°C/ min up to 600°C, held at this temperature for 30 min, and finally cooled to room temperature. The sample was then held at a desired isothermal temperature until thermal equilibration was reached (constancy of output signals), followed by introduction of oxygen to replace nitrogen at the same flow rate. Measurements were then started. The amount of heat released, Q , determined by the DSC technique, as well as the corresponding change in weight monitored by the TGA unit, W , were both measured as a function of time in oxygen. Values for the enthalpy of reaction, ΔH , were computed by knowing Q and W .

When Saran chars are exposed to oxygen at 100°C, chemisorption of oxygen is the only measurable process taking place. For the as-received char (150 x 250 mesh), ΔH scattered around 42 ± 1 kcal/mole of oxygen chemisorbed, being independent of reaction time, particle size, oxygen flow rate, and the original weight of char used. When the sample was air-activated by gasification to a 63.8% level of burn-off prior to the pretreatment procedure, ΔH was 75 ± 2 kcal/mole. Kinetics of oxygen chemisorption followed the equation

$$\text{Rate} = [k][f(\theta)][\text{ASA}][P_{O_2}] \pm I$$

where k , P_{O_2} , and $f(\theta)$ are rate constant, partial pressure of oxygen, and surface coverage (θ) factor, respectively. This latter term has the form $(1 - \theta)^2$ for the as-received char and $Z(1 - \theta)^2/(Z - \theta)^2$ for the air-activated sample (where Z is the number of adjacent sites shown to be equal to two). Values of activation energy (kcal/mole)

for the rate constant amounted to 11.3 ± 0.6 (independent of θ) for the former sample and ranged between 7.2 and 15.1 for the air-activated sample (dependent on θ).

At temperatures above 125°C, although the observed weight of chars was increasing with reaction time, chemisorption of oxygen is occurring concurrently with an "early"-gasification reaction. Amounts of carbon gasified and oxygen chemisorbed increase with reaction time. Rates of carbon gasification and oxygen chemisorption increase with increasing temperature up to 227°C. For the as-received char, the kinetics of either reaction followed the same equation given above. For the air-activated sample, kinetics of oxygen chemisorption at 100-227°C followed: (i) the previously mentioned equation and (ii) an Elovich type equation (W vs $\log$ reaction time).

Differential scanning calorimetry and thermogravimetric analysis were also used to study the interaction between seventeen coal chars and oxygen at 100°C. Values of Q (cal/g char) or W (mg/g char) were monitored for 30 min reaction time. Plots of Q or W versus $\log t$ were linear, thus conforming to an Elovich type equation ($dQ/dt = a \exp(-\alpha Q)$). At 15 min reaction time, the value of Q was used for the sake of comparison. Plots of Q_{15} versus the initial rate of heat released, a , were linear. Values of Q_{15} decreased asymptotically with: (i) α (the constant parameter of the Elovich equation), and (ii) carbon content of the parent coals from which the chars had been prepared. Increase of N_2 surface areas of chars was associated with an increase in Q_{15} up to 62 m²/g char. Thereafter, Q_{15} decreased with increasing surface area. Attempts were made to correlate values of Q_{15} to some available gasification data (for example, R_T and $\tau_{0.5}$,

where R_T is the maximum rate of gasification at temperature T and $\tau_{0.5}$ is the time required to gasify 50% of the char under consideration). For gasification in air of 405°C, Q_{15} first increases linearly with R_{405} and finally levels off. Further, Q_{15} decreases linearly with $\tau_{0.5}$. For gasification in steam at 910°C or in CO_2 at 900°C, Q_{15} decreases asymptotically with increasing $\tau_{0.5}$. Chars produced from a few acid washed and demineralized coal samples were considered. For these chars, although gasification rates decreased by an order of magnitude (or more), Q_{15} was only lowered by 20-100%.

In conclusion, the combination of measuring heats of oxygen interaction with chars (using the DSC technique) and weight changes during the interaction opens up a valuable new technique to characterize coal chars. Heats of interaction at 100°C are found to be related to rates of char gasification at higher temperatures. Both heats of interaction and gasification rates are, in turn, seen to increase sharply as the rank of coal from which the char is produced is decreased.

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1. INTRODUCTION

Considerable research and development activity in the United States has recently been devoted to the conversion of solid fossil fuels into more desirable clean energy forms, that is, synthetic gases and liquids. The commercial production of these fuels is currently hindered by a variety of complex and interacting factors, such as resource availability, protection of the environment, sociopolitical considerations, and of course, the possibility of wider availability of international supplies and lower cost natural gas and crude oil.

Strongly countering this situation is a growing realization of the long-term need for additional supplies of gaseous hydrocarbons as the United States enters an era in which depletion of conventional resources is a worldwide concern. Although recovery and conversion will be costly, the United States has substantial reserves (1560 billion tons) of coal (1) that can provide those synthetic fuels. This situation, together with a national goal of reducing dependence on imports, has, so far, led to increasing pressure for commercialization of synthetic fuels. This is far from a new concept. Gasification of coal, for example, has been commercially practiced on a worldwide scale since early in the 19th century. Coal liquefaction is currently practiced in some countries. However, most of this liquid production was, and continues to be, by Fischer-Tropsch synthesis, that is, from the coal-derived gases carbon monoxide and hydrogen. Thus, whether coal liquefaction or the production of synthetic gases from coals and chars is the goal, gasification reactions are of major importance. In fact, the terms "gasification" and "liquefaction" are not unrelated. Recent studies have shown a close

relation between the heat of hydrogasification for some coals and their liquefaction conversion factors, that is, percentages of liquified products for the coals (2). Heat of hydrogasification was measured by the DSC technique. In conclusion, gasification of carbonaceous materials, in general, and of coals and chars, in particular, are one of the national goals to be investigated.

Several studies have been conducted on gasification of carbonaceous materials and are reviewed by Von Fredersdoff and Elliot (3) and Walker et al. (4). These reviews showed that little attention had been paid towards understanding some of the fundamental thermal effects involved during gasification. This fact is also confirmed by the literature survey (Section 2.2.2). Because of the complex nature of this subject matter and due to the lack of reliable fast techniques which can be used to measure these thermal effects, investigators have been ignoring this field of study for many years. Recently, Mahajan et al. have studied some of the thermal effects involved during pyrolysis (5) and hydrogasification (6) of coals. Linares (2) has also been using the DSC technique in his attempt to correlate the DSC data for the heat of hydrogasification with the liquefaction conversion factors of some coals.

It seems complementary, therefore, to expand these thermal studies to the case where a carbonaceous material is interacting with an oxidant gas-air or oxygen. When a coal or char is allowed to react with oxygen, several reactions may occur. These include chemisorption of oxygen as well as the liberation of gasified products together with volatile matter (caking coals are excluded for the time being). Together with this are the possible reaction(s) between

oxygen and the noncarbonaceous components of the coal, that is, the mineral matter. Although compositions and structures of coals and chars are substantially different, they seem to have one common property towards gasification. The first step in the overall gasification process generally involves dissociative chemisorption of oxygen on the surface, the extent of which depends on several factors.

Among these are the type of coal or char used, particle size, reaction temperature, composition of the gas, presence of additives, and pretreatment conditions (if any). A reasonable study of these thermal effects involved during oxygen chemisorption on carbons could be directed either to investigate the effect of one of these many parameters on several coals and chars, or to consider the effect of all these parameters (or even more, if any) on one carbon. With the former possibility, however, it is believed that the study may be misleading. It could give a reasonable qualitative answer; however, the basic fundamentals of heat of oxygen chemisorption (for example, dependence of ΔH on pretreatment conditions or coverage) would not be clarified. With the second alternative, that is, the case of one specific carbon, a better understanding of the chemisorption process could be reached. The carbon has to be well characterized and its tendency to chemisorb oxygen ought to be high. Saran carbon, like coal chars, is a microporous material. It has been characterized by other workers in this laboratory (7).

Reactivities of coal chars were investigated by Jenkins et al. (8), where their reactivities in air at 500°C were defined as:

$$R_{500} = \frac{1}{W} \frac{dW}{dt} \text{ mg hr}^{-1} \text{ mg}^{-1} \quad 1.1$$

Values of R_{500} varied between 0.16 for an anthracite char and 4.0 for a lignite char (8). A similar reactivity run was made on a Saran char, where the value of R_{500} was found to be 0.6. This corresponds to a char carbonized from the parent coal which may have 79-80% carbon content (daf). The char could be located somewhere at the midway between chars prepared from lignites (about 70% carbon) and anthracites (94% carbon). The experiment thus supports the reasonable choice of a Saran carbon as a model to help the elucidation of the mechanism of oxygen interaction with microporous carbons.

2. LITERATURE SURVEY

2.1 ADSORPTION OF GASES ON SOLIDS

2.1.1 Physisorption and Chemisorption

When a fresh solid surface is exposed to a gas, the concentration of gas molecules at the surface is higher than in the gas phase. This preferential concentration of molecules at the surface is called adsorption. Apart from the nature of the gas solid system under consideration, the adsorption phenomenon is divided into two main types: physisorption and chemisorption. While the former is caused by forces of molecular interaction (van der Waals forces), chemisorption involves rearrangement of electrons between the gas and the solid; and, therefore, chemical bonds are formed. Three types of bonds are known: (i) the pure ionic, in which the adsorbate acts as an electron donor or acceptor; (ii) the pure covalent, embracing the coordinate link between the adsorbate and adsorbent; and (iii) the mixed type of bond. For chemisorption of oxygen on carbons, a typical covalent bond (9, 10) or mixed type of bonds (11) could be formed. The formation of a pure ionic bond has also been reported. Koutecky et al. (12, 13) have discussed the electronic structure of diamond and attempted to relate the existence of surface states to the normal bonds of the crystal lattice. They concluded that the (100) surface is characterized by lone electron pairs which tend to form donor-acceptor bonds with gas molecules.

2.1.2 Heat of Adsorption--Energy of Activation

The magnitude of the heat of adsorption is frequently used to differentiate between the two types of adsorption. During physical adsorption, the heat liberated is relatively small. For example, in

the case of ammonia-carbon system, heats reported range between 5.5-6.5 kcal/mole (14), and 6-7 kcal/mole (15). In the case of the inert gas-Graphon systems, the heat of adsorption varies between 0-9 kcal/mole, depending on the type of gas used, amount adsorbed, and reaction temperature (16). In the case of nitrogen physically adsorbed on an amorphous carbon, the heat of adsorption amounted to 1.5-3.7 kcal/mole depending on the fractional surface coverage (17). In addition, values as large as 20 kcal/mole for physisorption have been reported (18). On the other hand, for chemisorption reactions, larger values of heat of adsorption are usually found. These may vary between 40 and 200 kcal/mole. Sevenster (19), for instance, has reported that for the chemisorption of oxygen on some South African coals, a constant value of 67-70 kcal/mole was obtained at 0, 41, and 80°C. The value was independent of the amount of oxygen chemisorbed (19).

Since physical adsorption requires no activation, it occurs very rapidly. The activation energy of the process is known, in general, to be close to zero. For a chemisorption process, however, it requires activation; thus, the adsorption is likely to occur at a slower rate than that found for physical adsorption. This is not a rigid rule. On a microporous solid, physical adsorption may take place very slowly if diffusion of adsorbate along the pores is the rate determining step.

2.1.3 Potential Energy Diagrams (Depicting Adsorption)

Adsorption processes can also be described in terms of potential energy diagrams. For each adsorbent-adsorbate system, two general types of plots are included: a potential energy curve related to

physical adsorption and another curve related to chemisorption. Most adsorption processes are exothermic. However, a few endothermic adsorptions have been reported, that is, chemisorption of hydrogen on glass (18) and molecular oxygen (as O_2^-) on silver (20). These endothermic processes are emphasized elsewhere (21).

For the adsorption of oxygen on a carbon surface (exothermic), the general forms of the potential energy curves are shown in Figure 1. To the author's knowledge, none of these plots have been, so far, published because of the complexity of carbons and due to the lack of experimental data on the heats of chemisorption. The general shape of the potential energy diagram for interaction of molecular oxygen and atomic oxygen with a carbon surface are represented by curves X (path abcd) and Y (path ecfg), respectively. For physical adsorption, as an oxygen molecule approaches the carbon surface, the potential energy decreases until reaching point (b). A physically adsorbed oxygen molecule has the highest probability of being located at this distance from the carbon surface. Region (ab) corresponds to attractive forces, and the depth of (b) below the zero level corresponds to the heat of physical adsorption (ΔH_p). If the molecule further approaches the surface, path (bcd), repulsion forces commence becoming important as denoted by the potential energy passing through zero.

When an oxygen molecule is dissociated into two atoms, 118 kcal is required, as denoted by path (ae). When an oxygen atom approaches the surface from infinity, its potential energy first decreases, passes through (c), and finally reaches (f) where a stable carbon-oxygen complex is formed (9, 10). The depth of (f) below the zero level is the heat of oxygen chemisorption (ΔH_c). Also, it is known that molecular

Figure 1. Potential Energy Diagram for Carbon-Oxygen System

oxygen can be dissociatively adsorbed on the carbon without prior dissociation of the molecule in the gas phase. For this possibility, the path will be (abcf). Therefore, point (c) represents an intermediate activated state prior to the formation of the chemisorbed carbon-oxygen complex. Accordingly, the height of (c) above the zero level determines the value of the activation energy (E_a) for dissociative oxygen chemisorption.

Contrary to the case of a gas-metal complex, the carbon-oxygen complex desorbs through path (fhk), that is, curve Z. Once again, the stable complex has to reach an intermediate excited state (at h) before it converts to the gaseous product, that is, two CO molecules. The height (hm) represents the activation energy for desorption (E_d), while the length (ak) is the heat of reaction when one oxygen molecule reacts with two carbon atoms (β -graphite) to produce two molecules of CO. It is noteworthy that in the case of metals, desorption usually follows path (fcba), and therefore the difference in energy between point (c) and (f) corresponds to the activation energy for desorption.

In practice, when the carbon-oxygen complex is desorbed to CO and CO₂, the situation is rather complicated. The ratio CO/CO₂ depends on several factors. For a particular carbon, these factors are the fraction of the carbon surface covered by oxygen complex and the desorption temperature (22, 23).

Values of (ΔH_p) for physical adsorption of oxygen on different carbons are generally in the vicinity of 4-6 kcal/mole, that is, close to the heat of condensation of molecular oxygen. The values of (ΔH_c) for oxygen chemisorption on carbons are reported to vary between 51 and 145 kcal/mole (19-24). In fact, this kind of information does

not often appear in the literature. Apart from references (19, 24), most of the values reported are derived from studies conducted before 1940 (25-29).

2.1.4 Adsorption Isotherms

Relations showing the dependence of the amount of gas adsorbed on pressure at a constant temperature are known as adsorption isotherms. These are represented by equations relating how the concentration of adsorbed species varies with gas pressure. For physical adsorption of a gas on a solid surface, for example, adsorption of nitrogen on a carbon surface at -196°C , the Brunauer-Emmett-Teller (BET) equation (30) is applicable. The Dubinin-Polanyi equation (31) is used to describe the adsorption of CO_2 on carbons at room temperature. These equations are given in Section 4.1.3. Several other isotherms are presented in the literature. Some of these are mentioned below.

2.1.4.1 The Langmuir Isotherm

The Langmuir isotherm, which could be applied to both physisorption and chemisorption, was first derived on a kinetic basis of dynamic equilibrium between adsorbed molecules in the gas phase at a pressure P and adsorbed entities in the surface layer. The fraction of sites covered with the adsorbate, known as fractional surface coverage (θ), is given by

$$\theta = V/V_m = \frac{KP}{1 + KP} \quad 2.1$$

where V is the volume of gas adsorbed, V_m is the volume required to completely cover the surface with one monolayer of adsorbate, P is the equilibrium pressure of adsorbate in the gas phase, and K is the equilibrium constant, that is, the ratio between the rate constants

for adsorption (k_1) and desorption (k_2), respectively. This ratio is given, therefore, by

$$K = k_1/k_2 \quad 2.2$$

The original derivation of equation 2.1 and the assumption used for it are presented elsewhere (30, 31). The rate of adsorption is given by

$$\frac{dw}{dt} = k_1 P (1-\theta) \quad 2.3$$

where (w) is the amount of gas uptake at time (t). In the case of some solids and catalysts, in general, and for carbon surfaces, in particular, an additional parameter (A) is included on the right-hand side of equation 2.3. Here (A), usually designated as the active surface area (ASA), is the surface area active to a specific gas adsorption. Hence

$$\frac{dw}{dt} = k_1 P A (1-\theta) \quad 2.4$$

For chemisorption of oxygen on carbonaceous materials, equation 2.4 has been extensively used (32-37), where the role played by surface oxygen complex in the reaction kinetics of carbon oxidation has been illustrated. It was shown that the oxidation of Graphon, a high purity graphitized carbon black, takes place by the formation of a stable surface oxide (Section 2.1.3 and Figure 1), and the production of gaseous CO and CO₂. At temperatures in the range 575-675°C, the rates of disappearance of oxygen and formation of CO and CO₂ (determined mass-spectrometrically) were calculated. The steady state reaction rate, that is, $(-dP_{O_2}/dt)$ was given by an equation similar to 2.4.

With some carbons, chemisorption of oxygen may not be ascribed to the one site model of the Langmuir isotherm (equation 2.4). Walker et al. (38) and Bansal et al. (39) showed that for oxygen chemisorption on Graphon, the surface has discrete types of sites on which chemisorption takes place. Over the temperature range -78 to 160°C and at pressures between 7×10^{-4} and 7.6×10^{-2} Torr, five different groups of active sites were observed. Taylor and Thon (40) have observed the existence of two different groups of active sites for hydrogen adsorption on ZnO at 184°C. Electron spin resonance studies on the chemisorption of oxygen on a PVDC carbon at 100 and 120°C showed the existence of two groups of active sites (41). Chemisorption of hydrogen on an activated Graphon (activated by pre-oxidation in oxygen to 18.6% weight loss at 625°C) in the temperature range 80-600°C indicated the presence of four different groups of active sites on the carbon surface (42). For all these cases of multiple site chemisorption, the multisite Langmuir equation was used in the interpretation of the adsorption process. That is,

$$\frac{dw}{dt} = P[k_1A_1(1-\theta_1) + k_2A_2(1-\theta_2) + \dots + k_nA_n(1-\theta_n)] \quad 2.5$$

Usually as chemisorption is completed on one group of sites and then starts on a subsequent group of sites, the magnitude of the rate constant decreases. This indicates that for the first group of sites, the reaction has a fairly high rate, while on the last group of sites, the rate of gas uptake is slow.

2.1.4.2 The Freundlich Isotherm

The equation describing the Freundlich isotherm is given by

$$\theta = V/V_m = k P^n \quad 2.6$$

where $0 < n < 1$. The classical derivation of this equation was first

presented by Zeldowitch (43), then later by Laidler (44). For this isotherm, it is assumed that the surface sites are subdivided into several types; each type possesses a characteristic heat of adsorption. Following this assumption, Zeldowitch started with the one site model Langmuir equation 2.1 and applied it to the case where several sites were existing. An integral equation was obtained, the solution of which was only possible by making certain assumptions. One of these assumptions was that adsorption was occurring in the low coverage or θ range. This led to an approximate final form for the overall equation which could be represented by

$$\ln \theta = \frac{RT}{B} \ln P + \text{constant} \quad 2.7$$

where B is a constant. It is evident that equation 2.7 is similar to that given by Freundlich 2.6. This equation is regarded as a convenient form of the Langmuir equation at low pressures (cf. equation 2.1; as P approaches zero, the denominator becomes close to unity, and $\theta \approx k P^n$, where $0 < n < 1$).

2.1.4.3 The Tempkin (Slygin-Frumkin) Isotherm

This isotherm is given by

$$\theta = V/V_m = a + c \log P \quad 2.8$$

where (a) and (c) are constants. This equation, in its final form, was first proposed by Slygin and Frumkin (45) to describe a certain phenomenon, that is, a linear fall in heat of adsorption with increasing coverage (see Section 2.1.6). The equation was later found to be applicable to chemisorption of hydrogen on evaporated metal films (46) and of nitrogen on iron catalysts during the synthesis of ammonia (47).

2.1.5 Kinetics of Adsorption--Elovich Equation

The Elovich equation is widely applicable for many gas-solid systems and is a convenient way to describe the kinetics of chemisorption. The equation, in several instances, has been used to calculate the activation energy of the adsorption. In its differential form, the equation is written as

$$\frac{dw}{dt} = a \exp (-\alpha w) \quad 2.9$$

where (w) is the amount adsorbed at time (t); (a) and (α) are constants for each system but may vary with temperature (48-50).

The integral form of 2.9 is given by

$$w = \frac{1}{\alpha} \ln (1 + a\alpha t) \quad 2.10$$

which is similar to

$$w = \frac{1}{\alpha} [\ln (t + t_0) - \ln (t_0)] \quad 2.11$$

where $t_0 = 1/a\alpha$. It is seen, therefore, that if the plot of $\log (1 + a\alpha t)$ versus (w) or $\log (dw/dt)$ against (w) is linear, the Elovich equation is obeyed. Much adsorption data for gases on metals were described by this equation. The applicability of the equation serves three main purposes. Firstly, it provides a convenient method of graphing and interpolating the data. Secondly, it permits calculations of instantaneous rates of adsorption by graphical evaluation of the intercept and then back substitution in the original equation. Thirdly, if both physical adsorption and chemisorption processes are occurring simultaneously, the equation provides a means of extrapolating the data to determine the initial rate of chemisorption which cannot be measured experimentally because of the simultaneous physical adsorption process.

Experience has also shown that when the experimental results do not conform to either equation 2.9 or 2.10, equation 2.11 could then be used. It has been suggested (40) that the term (t_0) may arbitrarily be selected to give a linear plot of (w) versus $\log (t + t_0)$. Furthermore, in some cases, the plots were found to be discontinuous (38-42), that is, at a certain value of t there exist one or more breaks in the w - $\log t$ plots. This is not only true with carbons. Discontinuities in the plots were earlier observed by Sickman and Taylor (51) and Strother and Taylor (52) for desorption of hydrogen on ZnO and by Maxted and Moon (53) for adsorption of hydrogen on platinum. For oxygen chemisorption on different carbonaceous materials, two conflicting findings have been reported. With some carbons the Elovich plots are continuous over the entire time interval studied, while with other carbons, discontinuities are observed with one to four breaks. Both cases are here reviewed.

2.1.5.1 Continuous Elovich Plots

Sevenster (54) has studied the interaction of oxygen with some South African coals in the temperature range 0-90°C. Basically, he considered the kinetics of oxygen chemisorption on these coals. Five coals (A, B, C, D, and E) having carbon contents (air dry basis) of 43, 45, 55, 58, and 62%, respectively, were considered. Adsorption isobars were constructed by using a constant pressure apparatus (19) where the volume of oxygen chemisorbed was followed as a function of time up to 100 hours. This interaction was divided into three phases. The first phase had an overall rate determined mainly by a chemisorption process, while the final phase of slow adsorption was represented by a parabolic diffusion equation (55). The latter finding indicated

that slow diffusion of oxygen was occurring through the pores of the coal. The second phase was then considered as an intermediate state between the first and last phases. For the initial phase, that is, during the first 25-30 minutes reaction time, the Elovich equation was applicable. Values of (a) and (α) were calculated for each coal at different temperatures, simply by making suitable choices of (t_0) . For coals A, B, C, and D, one general trend was observed, that is, as the temperature increased from 30 to 90°C, values of (α) decreased while those of (a) increased. Coal E gave some erratic behavior which could not be explained.

The author concluded that under the experimental conditions used, chemisorption of oxygen was the only predominant process. However, in his attempt to calculate the activation energy of the process (55), three values were reported for each coal, corresponding to three temperature regions: 30-50°C, 50-70°C, and 70-90°C. Values of E_a for the second region were about half or less than those obtained in the first region. These values of E_a varied between 1.9 to 10 kcal/mole, depending on the type of coal and the region of temperature, as well as on the amount of gas adsorbed. The author concluded that at 30-50°C, chemisorption was very low and that the rate of transport of gas molecules to the surface was relatively so high that this transport would not exert a retarding effect on the overall process. In the temperature region 50-70°C, the rate of chemisorption increased much faster with rise in temperature than that of the diffusion process; therefore, the activation energy is shown to be lowered. With further temperature increase (70-90°C), a point was reached beyond which diffusion became the slower and, hence, the rate determining step.

This observation on activation energies was different than that found by Carpenter and Sergeant (56), who studied the initial stages of oxidation of two South Wales coals at 37-105°C. Coals A and B had carbon contents of 64 and 91% (air dried basis). The samples were first outgassed and then flushed with nitrogen at a given temperature. A mixture of oxygen and nitrogen (ratio 10:90) was then introduced over the sample to a gage pressure of 700 Torr. A flow rate of 50 cc/min was maintained over the sample. The outlet gases were first passed through absorption tubes to remove CO₂ and water vapor, and then passed to an oxygen analyzer, where the oxygen content of the effluent gas was determined. The amount of oxygen uptake was then calculated at different time intervals. For both coals, the Elovich plots were linear over a reaction time of 10 minutes. The estimated value of (t_0) was almost constant and amounted to 2 minutes. This value was independent of reaction temperature in the range 37-105°C. For coal A, values of (E_a) increased with the extent of oxidation and also with increasing particle diameter. These values ranged between 1.7-6.2 kcal/mole.

It is noted, therefore, from the work of Sevenster (54) and Carpenter and Sergeant (56) that the linearity of Elovich plots were only true for short periods of time (up to about 10 minutes). The authors have not shown whether this linearity was applicable for longer periods of oxidation. In spite of this fact, it is evident from both works that during the oxidation of different coals up to 100°C, chemisorption of oxygen is the rate determining step.

On the other hand, the work of Allardice (57) on a brown coal char showed that linearity of the Elovich plots could be observed for

reaction times up to 5 hours. The author emphasized that physical adsorption affects the plots. This effect was not taken into consideration by other authors (54, 56). Allardice studied the adsorption of oxygen on degassed brown coal char in the temperature range 25-200°C at pressures up to 1 atmosphere. The weight of oxygen uptake was determined gravimetrically by using a modified McBain-Baker sorption balance. The amount of physically adsorbed oxygen was determined at several pressures and temperatures. This amount was found to decrease upon raising the temperature (at a fixed oxygen pressure) or upon lowering the pressure (at a given temperature). At a fixed value of pressure and temperature, the total weight of oxygen uptake (w_t) was determined at different time intervals. At the end of runs, the samples were isothermally evacuated at 1000°C for 10 hours. The amount of oxygen physically adsorbed (w_p) was then determined. The difference between (w_t) and (w_p) was expressed as the weight of oxygen chemisorbed. These weights were used to construct Elovich plots. For all reaction temperatures studied, parallel lines were obtained over 300 minutes reaction time. At 65°C, a set of plots was constructed at different pressures of oxygen. Straight lines were also obtained, the slopes of which, however, increased with increasing pressure. Values of (α) decreased from 1.65 to 1.07 as the pressure increased from 161 to 760 Torr. The activation energy obtained was 11.1 ± 1.5 kcal/mole and independent of coverage. This low value of E_a was attributed to rate control by migration of a mobile physically adsorbed layer across the surface to active sites where chemical interaction occurred. The fact that the activation energy was independent of surface coverage (57) also supported the assumption that the rate was controlled by surface migration.

In this case, the activation energy should depend only on the energy barrier between adjacent adsorption sites, irrespective of the amount of oxygen chemisorbed.

Normally, chemisorption conforming to the Elovich equation has activation energies increasing with coverage (40). However, some examples of constant activation energy have also been reported (58, 59). Walker et al. (59) studied the kinetics of oxygen chemisorption on spectroscopic grade, highly crystalline natural graphite at an oxygen pressure of 760 Torr and temperatures between 335 and 448°C by measuring the change in thermoelectric power of the graphite as chemisorption proceeded. The rate constant was independent of surface coverage.

2.1.5.2 Discontinuous Elovich Plots

Discontinuities in the Elovich plots were earlier observed by Deitz and McFarlane (60) for adsorption of oxygen on evaporated carbon films of high surface areas at 100-300°C and a pressure of 0.1 Torr. A rapid initial adsorption followed by a much slower adsorption was observed. The slow step was attributed to physical adsorption, the kinetics of which followed the logarithmic rate law and a first order dependence on pressure. In fact, Allardice (57) noted a similar two-stage adsorption; however, "his" chemisorption data conformed to the Elovich equation.

Lussow and co-workers (61, 62) conducted their experiments on chemisorption of oxygen on preoxidized Graphon samples in the temperature range 300-625°C at 0.5 Torr oxygen pressure. At temperatures above 400°C, a sharp increase in the amount of oxygen adsorbed was observed, thus suggesting the presence of two types of active sites.

These carbon samples were cleaned at 950°C in a vacuum of 10^{-5} Torr. However, when the samples were cleaned at 950°C in a vacuum of 10^{-8} Torr (37), more active sites were observed at oxygen pressures ranging between 0.001 and 0.015 Torr. Hart and co-workers concluded that adsorption of oxygen was dissociative (path abcf, Figure 1) and the rate was proportional to the square of the concentration of uncovered active sites. The activation energy of adsorption on the more active sites was 7.4 kcal/mole.

The study was then expanded (38) where chemisorption of oxygen on an ultraclean Graphon surface at room temperature (25°C) and at different starting pressures of oxygen (7×10^{-4} - 7.6×10^{-2} Torr) was considered. Elovich plots were discontinuous straight lines, indicating the existence of different kinetic stages. Each of these appeared after adsorption of a definite amount of oxygen (independent of pressure) and corresponded to adsorption on a different group of active sites. In all, five groups were observed at room temperature. For stages I, II, III, IV, and V, weights of oxygen chemisorbed were $(1.25 \pm 0.06, 1.40 \pm 0.04, 3.42 \pm 0.06, 8.41 \pm 0.8, \text{ and } 11.4 \pm 0.3) \times 10^{-18}$ atoms/g C, respectively.

This investigation was once more expanded (39) to study chemisorption of oxygen on ultraclean Graphon in the temperature range of -78 to 160°C at 0.1 Torr starting pressure. Over the entire temperature range, the findings were similar to those (38) reported earlier (five groups of active sites). Furthermore, increasing temperature (for a given oxygen pressure) or pressure (at a given reaction temperature) resulted in an earlier appearance of any one kinetic stage. At -78°C, chemisorption occurred on stage I followed by II. At 25°C,

three stages appeared (I, II, and III), while at 55°C, the first stage was not observed (it was too rapid). Instead, a less active group of sites appeared (stage IV). At 90 and 125°C, four stages were observed, that is, II, III, IV, and V. At 160°C, stage II was not observed, and no additional group of sites appeared. For each stage, it was noted that (α) was independent of temperature, while values of (a) increased with increasing temperature. Values of (α) scattered around 5, 2, 0.65, 0.41, and 0.34 for stages I, II, III, IV, and V, respectively. Activation energies averaged to about 3.1, 7.2, 9.5, 10.5, and 12.4 kcal/mole for the five regions respectively. It was concluded (39) that each linear region represents adsorption on different discrete type of sites on the Graphon surface.

The work of Seymour and Wood (41) indicates the existence of active sites on a polyvinylidene carbon (PVDC). The electron spin resonance technique was used to study the interaction between carbon surface and oxygen. PVDC is known to have a high free radical concentration and a high reactivity towards oxygen (a paramagnetic gas) (63). Variation of spin center concentration may be caused by heat treatment or by exposing the carbon to gases such as oxygen (41, 63). Combining spin concentration measurements with gravimetric studies permitted the authors (64) to calculate the number of spin centers destroyed per oxygen molecule adsorbed. This combination allowed calculation of heat of physical adsorption of oxygen on the carbon.

The authors expanded the previous studies in an attempt to calculate activation energy and to characterize the rates of the adsorption process (41). Experiments were performed at an oxygen pressure of 2.4 Torr in the temperature region of 30-120°C. The results conformed to

the Elovich equation with no necessity for linearizing factors (t_0). Discontinuities were also observed, thus indicating that adsorption was occurring successively on sites having different activation energies. For these plots, the percentages of spin disappearance (could be looked at as the weight of oxygen chemisorbed) were plotted versus ($\log t$). Three kinetic stages were observed. The first region ended after 5 seconds; therefore, no further conclusions could be reached. This was attributed to physical adsorption of oxygen on PVDC. The second and third regions were attributed to chemisorption. For the second region, parallel Elovich plots were obtained at all temperatures, thus, indicating a zero activation energy process. The third region, however, gave an activation energy of 4.7 kcal/mole. The authors noted that additional discontinuities appeared at higher temperatures, and the reaction seemed to be more complicated.

X-ray induced photoelectron spectroscopy (XPS) was used to study oxygen chemisorption on the basal faces of single crystals of graphite (65). After the sample was cleaned at pressure below 10^{-9} Torr, molecular oxygen (10^{-4} Torr) was introduced. The amount of chemisorbed oxygen at 400°C determined via XPS signals was small. Under the same experimental conditions, the degree of oxygen uptake was considerably enhanced when the basal face had previously been bombarded with argon ions prior to chemisorption. This was attributed to the creation of vacancies induced by the bombardment which, in fact, meant an increase in the number of active sites existing at the basal face.

Atomic oxygen was also chemisorbed on the graphite surface at 400°C (64). The plots of the amount adsorbed versus $\log t$ showed two

distinct regions of linearities. It was concluded that for chemisorption of oxygen on the basal surface of graphite, at least two different types of bonding would exist. This conclusion is further considered in Section 2.1.8.

2.1.6 Dependence of Heat of Adsorption on Surface Coverage

Basically, there are three different views describing the dependence of heat of adsorption, ΔH (kcal/mole adsorbate) on the value of surface coverage (θ). The Langmuir theory assumes that the heat of adsorption remains constant with increasing values of (θ), but there is little evidence supporting this assumption (66). In most cases, direct determination of ΔH - θ dependence reveals a decrease in ΔH with an increase in θ . The Freundlich equation assumes that the fall in heat of adsorption with increasing θ is logarithmic. This may introduce the idea that adsorption sites are distributed exponentially with respect to the heat of adsorption. Thus, the surface sites are subdivided into several types, each of which possesses a characteristic heat of adsorption. On the other hand, the Temkin isotherm assumes that the fall in ΔH - θ plots is linear. This linearity may arise either from repulsion between adsorbate species on a uniform surface or from intrinsic surface heterogeneity.

It may be generalized, though not firmly, that whenever a plot of $\log P$ versus θ is linear, the heat of adsorption falls linearly with increasing θ . In addition, if a linearity exists between θ and P , the fall between ΔH and θ is logarithmic. As an example, the heats of adsorption of hydrogen on several metals (67) can be considered. In the case of Rh, ΔH decreases linearly from 27 to 22 kcal/mole for θ between 0.0 and 1.0. In the case of Ta, as θ increases from 0.0 to 1.0,

ΔH falls logarithmically from 38 to 10 kcal/mole. With W, however, ΔH first decreases logarithmically from 45 to 35 kcal/mole (θ goes from 0.0 to 0.6), it essentially remains constant for θ between 0.6 and 0.8, and finally drops abruptly to 10 kcal/mole as θ goes to one.

An increase in heat of chemisorption with increasing coverage has also been reported. Boudart (68) postulated that in the case of semiconductors, chemisorption is accompanied by an electron transfer from chemisorbed species to the solid adsorbent, or vice versa. As a result, an ionic chemisorption bond is not necessarily formed, in fact, all intermediate states between covalent and ionic bonds are possibly formed. According to the direction of electron transfer, the chemisorbed species behaves as a donor or as an acceptor. Therefore, at constant temperature, if the chemisorbed species are electronegative (acceptor), the Fermi energy level of the semiconductor decreases upon increasing the concentration of adsorbed species. Therefore, the heat of adsorption would increase with increasing concentration, that is, with surface coverage. On the other hand, if the chemisorbed species are electropositive (donor), the Fermi energy level increases and the ionization of donor decreases. Accordingly, heat of adsorption is expected to decrease with increasing coverage. This effect was named "induced heterogeneity" (68).

Heats of adsorption can be determined either by direct calorimetric measurements (isothermal and adiabatic heats of adsorption) or indirectly by applying the Clausius-Clapeyron equation to a series of adsorption isotherms (isotheric or differential heats of adsorption). The former approach is further described by Section 2.2. For the indirect determination of isosteric heat of adsorption, $(\Delta H)_{iso}$, a

series of adsorption isobars are first obtained experimentally at different adsorption temperatures. From these plots, a given value of θ is chosen. The corresponding equilibrium pressures at different temperatures are then obtained from the plots. A second plot, that is, $\ln P$ versus reciprocal of absolute temperature, is then constructed. When the plots are linear, the results conform to the Calusius-Clapeyron equation:

$$\left(\frac{\partial \ln P}{\partial T} \right)_{\theta} = \frac{(\Delta H)_{iso}}{RT^2} \quad 2.12$$

and

$$\ln P = - \frac{(\Delta H)_{iso}}{R} \cdot \frac{1}{T} + \text{constant} \quad 2.13$$

Therefore, values $(\Delta H)_{iso}$ can be determined at particular coverages.

In some cases, for accurate determination of $(\Delta H)_{iso}$, the variation of $(\Delta H)_{iso}$ with adsorption temperature may not be neglected. If this is the situation, a correction factor has to be introduced. This includes the difference in partial molar heat capacities, ΔC_p , of the adsorbate in the gas phase and in the adsorbed state. Usually, Kirchhoff's equation is used to make this correction:

$$(\Delta H)_{iso} = (\Delta H)_{iso}^{\circ} + \int_0^T \Delta C_p \, dT \quad 2.14$$

where $(\Delta H)_{iso}^{\circ}$ is the heat of adsorption at absolute zero.

At this stage, little is known about the nature of species in adsorbed state. At relatively low temperatures, the adsorbed molecule might be localized and vibrationally unexcited. Therefore, it has no translational, vibrational or rotational degrees of freedom. If the original molecule in the gas phase is assumed to be diatomic, each molecule will have three degrees of translational freedom, plus two degrees

of rotational freedom, so that C_p is about $7R/2$. For the adsorbed atoms at a relatively high chemisorption temperature, each of the atoms will have a heat capacity made up of $2R/2$ from translational, $2R/2$ from vibrational, thus making C_p the order of $6R/2$. Therefore, for the extreme case when the diatomic molecule in the gas phase is not vibrationally excited, ΔC_p will amount to $-5R/2$. It follows, therefore, that for no other reason than the change in heat capacities, a diminution in the value of $(\Delta H)_{iso}$ of about 5 cal/mole can be expected while raising the temperature to a region in the vicinity of $1000^\circ K$.

2.1.7 Relations between Heats of Adsorption and Heats of Formation

As mentioned in Section 2.1.2, evidently there is a parallelism between heat of adsorption and the nature (strength) of the bond formed. As a consequence, it is expected that when this observation is further considered, an empirical equation relating the heat of adsorption and that of formation of the corresponding compound may be predicted. This kind of information might vary from one system to another; yet it throws some light on the nature of adsorption. Brennan and co-workers (69), for example, have noted a close similarity, in a number of instances, between the heat of oxygen chemisorption on evaporated metal films and the heat of formation of the corresponding bulk metal oxides. Furthermore, during catalytic decomposition of formic acid on metals, there appears to be a definite correlation between the catalytic activity of the metal and heat of formation of the metal formate (70, 71). Roberts (72) showed that heat of formation of many metal oxides, nitrides, hydrides, and sulphides varied smoothly with the heat of adsorption of the corresponding gases (on the surface of metals), that

is, oxygen, nitrogen, hydrogen, and hydrogen sulphide, respectively, on these metals.

Tanaka and Tamaru (73) have formulated a general rule relating the initial heats of chemisorption ΔH_C of oxygen, ethylene, nitrogen, hydrogen, and ammonia on various metals to the standard heat of formation (ΔH_f°) of the highest oxide/metal atom. This is given by

$$\Delta H_C = a [(-\Delta H_f^\circ) + 37] + 20 \text{ kcal/mole} \quad 2.15$$

where a is a constant that depends on the nature of gas chemisorbed. The authors (73) first showed linearities between values of ΔH_f° (for some metal oxides) and the corresponding standard free energies of formation (ΔG_f°). These oxides were Ag_2O , PdO , CuO , K_2O , Na_2O , NiO , Li_2O , ZnO , Fe_2O_3 , MnO_2 , SrO , Cr_2O_3 , MgO , BeP , CaP , V_2O_5 , WO_3 , Al_2O_3 , TiO_2 , and ThP_2 . Other linearities were also observed between ΔH_f° and the corresponding standard heats of formation of either the hydroxides, the sulphates, the formates, or the nitrates. It was then concluded that heats of formation of metal compounds were following a definite order according to one given pattern by which the metals were arranged. Although this order was independent of the type of compound under consideration, the slopes and intercepts of the lines varied from one compound to another. This observation was attributed to differences in the nature of electronegative groups with which metals were combined.

The authors (73) then studied a possible correlation between heats of chemisorption of gases (on the same metals) and heats of formation of surface compounds. Taking the data for initial heats of chemisorption, ΔH_C , of oxygen (69), ethylene (71), hydrogen (74), nitrogen (67, 75, 76), and ammonia (77) on these evaporated metal films and relating them to ΔH_f° for the highest oxide, the authors (73) concluded that for

each gas the plot of ΔH_C versus ΔH_f° was linear and basically independent of the type of metal. Depending on the type of gas being chemisorbed, the slopes of lines, that is values of a increased in the following order: $O_2 > N_2 \sim C_2H_4 > NH_3 > H_2$. These values amounted to 0.789, 0.395, and 0.079 for oxygen, nitrogen, and hydrogen, respectively. This order was shown to be in accordance with the values of electronegativities for these gases.

It is interesting to reformulate equation 2.15 and consider the case of oxygen chemisorption on a carbon. Taking a value of 0.789 for the parameter a and substituting in the equation, one gets

$$-(\Delta H_f^\circ)_{C-O} = 1.27 (\Delta H_C)_{C-O} - 45.4 \quad 2.16$$

Equation 2.16 could be useful in predicting the value for the heat of chemisorption of oxygen on carbons.

The work of Brennan et al. (69) is also significant. Values of ΔH_C for oxygen chemisorption on evaporated films of Ti, Cr, Mn, Fe, Co, Ni, Nb, Mo, Rh, Pd, Ta, W, Pt, and Al were related to the oxygen/metal ratios as well as to the heats of formation of certain corresponding oxides. For the first six metals, the difference between ΔH_f° of the corresponding oxides (Ti_3O_5 , Cr_2O_3 , Mn_2O_3 , Fe_3O_4 , Co_3O_4 , and NiO) and the values of ΔH_C for oxygen chemisorption were $\pm 3\%$. However, for the latter eight metals, values of ΔH_C and ΔH_f° were exceptionally different, yet they had the same order. Thus, an increase in ΔH_f° from 34 kcal/mole for PtO to 193 kcal/mole for Ta_2O_5 was associated with an increase in ΔH_C from 67 to 212 kcal/mole. Furthermore, the authors found two linearities between ΔH_C and the atomic radii of the metals. For Ni, Mn, Cr, Mo, Nb, Al, Ta, and Ti, as the atomic radius increased

from 1.24 Å (Ni) to 1.47 Å (Ti), ΔH_C increased from 100 to 236 kcal/mole. On the other hand, for Co, Rh, Pd, and Pt, as the atomic radius increased from 1.25 Å (Co) to 1.39 Å (Pt), ΔH_C decreased from 100 to 67 kcal/mole.

2.1.8 Surface Complexes Formed During Adsorption of Oxygen on Carbons

The properties of surface complexes formed between oxygen and carbons or graphites have been investigated by several authors. Detailed literature surveys on this subject matter have been written by Boehm (78) and Donnet (79). However, a special emphasis is given here to summarize a few articles which appeared to be relevant to the work of this thesis.

For a given carbon, surface atoms are known to have unsaturated valencies able to bond with other elements, molecules, or compounds to form a complex(es). This bonding could vary from the simplest case of a physically adsorbed monolayer to a rather complicated state of chemisorption.

Several attempts were made to examine the nature of this bonding when carbons and oxygen interact together. For example, over a century ago, Smith (80) reported that carbon surfaces could have some kind of surface oxides which were desorbed by heating as CO_2 . Baker (81) showed that when carbons react with oxygen at -13°C , more than one carbon-oxygen complex was formed. A similar observation was confirmed more recently by Zarif'yanz et al. (82). Two carbon-oxygen complexes were formed at -40°C . The oxides were removed as CO_2 and CO at desorption temperatures above 200°C . Electrokinetic potential studies on oxidized carbons showed that they could possess either acidic or basic properties depending on the oxidation temperature (83, 84). Acid

surface oxides are formed when the carbon reacts with oxygen at high temperatures (85). Basic oxides are formed during lower oxidation temperatures (86). It has also been reported that carbons activated at temperatures above 500°C are basic (87), while those activated at lower temperatures are essentially acidic (84, 88, 89). Basic carbons [sometimes referred to as "H" carbons (89)] interact with acidic solutions in a way which involves an anion. They are characterized by their ability to raise the pH of neutral or acidic solutions and also by being hydrophobic. The properties of these basic surface oxides are, for the most part, unknown. Garten and Weiss (88, 90) have proposed some structures for these oxides. Rivin (91) was only able to prove the existence of cationic surface sites on carbon blacks treated with oxygen.

Acidic carbons [referred to as "L" carbons (89)] are known to lower the pH of a neutral or alkaline solution. These carbons are generally hydrophilic. Their acidities were earlier attributed to the existence of carboxyl groups bound to the surface (92, 93). Other functional groups have been more recently identified. In brief, there are four major groups--the carboxylic, the hydroxyl (phenolic), the carbonyl, and the lactones (65).

Several chemical tests were used to identify the existence of functional groups on oxidized carbon surfaces. For example, the presence of carboxylic groups was confirmed by direct titration with alkalis, carbonates, bicarbonates, and acetates (94-98), formation of acid chlorides (99), reaction with dimethyl sulphate (100, 101), decarboxylation above 600°C (94), reaction with lithium aluminum hydride (102), and isotopic exchange for the hydrogen atom of the carboxyl group (103).

Phenolic hydroxyl groups were identified by their reaction with dinitrofluorobenzene or paranitro benzoyl chloride (96, 98). In some cases, organo magnesium halides (known as Grignard reagents, RMgX) were used to identify hydroxyl as well as carboxyl groups (104). Two different products were identified, The $-\text{OMgX}$ and the $-\text{OOMgX}$, respectively.

Carbonyl groups have been identified after they were catalytically hydrogenated (in the presence of Pt) to form the corresponding phenols (105, 106). These groups were also characterized by condensation with aniline (107), or their reactions with hydroxylamine (103). Further chemical tests are described elsewhere (107, 108).

Lactones were identified by specific reactions including the addition of ammonia or hydrobromic acid (103), or the reaction with lithium aluminum hydride (94).

Several attempts were made to correlate the nature of functional groups, formed during the oxidation of carbons, to the amount of CO and CO_2 evolved during subsequent pyrolysis in inert atmospheres. Rivin (109) suggested that CO_2 was usually derived from carboxyl and lactone groups (containing two oxygen atoms), while the hydroxyl and carbonyl groups (having one oxygen atom) decomposed to give CO. Bonnetain and Hoynant (110) concluded that both gases were derived from the same surface sites. Puri (111) was able to correlate the amount of evolved CO_2 with alkali neutralized by the carbon surfaces. For a large number of carbons, one mole of CO_2 evolved corresponded to two equivalents of alkali neutralized. The author concluded, therefore, that there were no carboxyl groups at the carbon surface, instead " CO_2 complexes" of unknown structure were bound to the surface. For all

other chemisorbed species of oxygen, they desorbed as CO. Heck (112) and Boehm et al. (96, 100, 113) added valuable information to this subject matter. A convenient way for quantitative determination of acid groups is their reactions (neutralizations) with bases of varying strengths. For example, 0.05 N NaHCO_3 reacts with carboxyl groups, 0.05 N Na_2CO_3 opens lactone rings and neutralizes the carboxyl groups, 0.05 N NaOH reacts with hydroxyl as well as carboxyl and lactones, and 0.1 N alcoholic NaOEt solution reacts with all groups together with the carbonyls (111). Thus, by simple subtractions, each functional group was determined separately. These reagents were used to study oxygen surface complexes formed on some commercial carbons and charcoals (111, 112). Prior to oxidation, the charcoal was either heat treated in N_2 up to 1100°C (sample A) or it was activated in CO_2 at 950°C to a 40% level of burn-off (sample B). After each sample was reacted with oxygen at 420°C , chemical analyses were made to quantitatively determine the four major functional groups. Isothermal desorption runs were then made in an inert atmosphere in the temperature range $440\text{--}550^\circ\text{C}$ for sample A and $380\text{--}900^\circ\text{C}$ for sample B. Weights of evolved CO and CO_2 during each desorption run were also measured. At the end of desorption, the samples were cooled. Once more, chemical analyses for acid groups left on the surface were made. By subtraction from the total, the decomposed functional groups lost during desorption were quantitatively computed. Attempts were made to examine the dependence of the amounts of functional groups which decomposed to the corresponding CO and CO_2 evolved (112, 113). For sample A, the CO_2 evolution was almost equal to the sum of the losses in carboxyl, lactone, and carbonyl groups. For sample B, the CO_2 liberated was only

equivalent to the losses in carboxyl and carbonyl groups. Other carbons showed different behaviors. However, in all cases studied, the total oxygen content in CO and CO₂ was higher than the corresponding sum of the oxygen content accounted for in the four major functional groups.

The authors (113) concluded that no firm conclusion could be drawn. The rules were different from one carbon to another. Even for one carbon, pretreatment conditions as well as desorption temperature after oxidation, play a major role in determining these functional groups. Apparently, the transformation from one functional group to another is most likely to happen during desorption treatment. The authors also (112, 113) noted that invariably: (i) the concentration of carboxyl functional groups decreases with increasing desorption temperature, and (ii) the evolved CO or CO₂ increased with desorption temperature.

Paralleling the observation obtained with chemical tests, IR spectroscopy on oxidized carbons has shown spectra having characteristic bands for carboxyl, lactone, hydroxy, and carbonyl function groups (111-117). Smith *et al.* (117) studied the surface complexes formed when very thin hydrogen-free carbon films were reacted with O₃, O₂, NO, N₂O, CO₂, and H₂O₂ at different reaction temperatures and pressures. In all cases, three major peaks of different intensities were observed at 1754.4, 1562.5, and 1351.4 cm⁻¹. These were attributed to carbonyl, lactone, and hydroxyl, respectively. In the absence of H₂O₂, the 1351.4 cm⁻¹ peak was attributed to the carbonyl group. When the carbon was reacted with O₂ (100-500 Torr) at room temperature, the three peaks appeared slowly and were weak. In the temperature range 450-500°C,

the peaks appeared rapidly and were strong. In addition, the 1754.4 cm^{-1} peak (for carbonyl) became stronger than the 1562.5 cm^{-1} peak when CO_2 started evolving. The authors concluded that the two oxygen atoms which evolved in the CO_2 in the combustion of carbon came exclusively from two different oxygen molecules. They suggested that the carbon film had successive layer planes, each of which was a series of complete and incomplete six membered rings. The latter gave rise to a number of carbon fragments (say 1- and 2-) extending out of the plane. When one end of an oxygen molecule attacks, more likely, one of these fragments, there would be a combined length of C-O-O or C-C-O-O groups (117). The terminal oxygen atom may attack another carbon (say 4- or 5-) in the same plane to form 5- or 6- membered lactone rings. Obviously, it was assumed that the second carbon atom had already formed a carbonyl group with a different oxygen molecule. The terminal oxygen atom could also attack a carbon atom in another plane. Subsequent breakage of the O-O bond led to the formation of two carbonyl groups on two different planes. As each of the lactone groups kept forming from two different oxygen molecules, a state is reached above which these groups started breaking to evolve CO_2 .

When the carbon was reacted with O_3 (1 atm) at room temperature, the 1754.4 cm^{-1} peak (carbonyl) was the major strong peak appearing in the spectra. The other two peaks (lactone) were weak. Thus, oxygen atoms were mainly forming carbonyl groups. In order to explain gasification of the carbon with O_3 , the authors (117) suggested that each carbonyl group was attacked by "another" oxygen atom produced from "another" O_3 molecule decomposing at the carbon surface ($\text{O}_3 \rightarrow \text{O}_2 + \text{O}$).

It is noteworthy to state that the previous mechanism is different than that proposed by Lussow et al. (61). The authors suggested that an oxygen molecule may react with the carbon surface to form mobile transition state complexes which upon dissociation may give two mobile chemisorbed oxygen atoms. The chemisorbed species may either react to form a relatively stable surface oxide or it may directly give CO and CO₂.

Infrared spectroscopy, like chemical tests, does not confirm a relation between functional groups formed on the carbon surface and the nature of gasified products. The technique is limited since it suffers from a strong absorption by carbon, which in turn weakens the absorption peaks.

More recent techniques have been developed to explain our understanding of the chemistry of complexes formed on carbon surfaces. These include photoelectron spectroscopy and internal reflectance spectroscopy. The modified technique of conventional IR spectroscopy is called internal reflectance spectroscopy (IRS) (118-120). Applications of IRS to the cases of powders having high optical densities (121) and those of activated carbons (122-125) have also been reported. Selected results are now reviewed.

Activated sugar chars were first prepared by carbonizing dextrose in air at 600°C for 6 hours (124). The product was further activated under two different controlled atmospheres--1% O₂ - 99% N₂ (Series 1), or 5% O₂ - 45% CO₂ - 50% N₂ (Series 2). Activation temperatures were 300, 400, 500, 600, and 700°C. The IRS for both series showed characteristic bands at 1750-1770, 1710-1750, 1620-1690, 1590-1625, 1510-1560, and 1140-1230 cm⁻¹. For each spectrum, the relative intensities of

bands were used for comparison with another spectra. For series 1, the first two bands were attributed to the presence of a pair of adjacent carboxyl groups at the edges of basal planes of carbons.

Those bands observed at 1590-1625 and 1510-1560 cm^{-1} indicated the presence of quinone (1, 4 position) carbonyl groups. The relative intensities of these two bands increased with the temperature at which samples had been activated up to 500°C. Passing through a maximum (around 500°C), these intensities decreased with activation temperatures of 600 and 700°C. This sequence of relative intensities and activation temperatures was similar to that obtained for adsorption capacities of paranitrophenol on the carbons versus their activation temperatures. It is known that paranitrophenol is an electron accepting compound, while carbonyl groups are electron donor groups. Therefore, an increase in adsorption capacity of paranitrophenol indicates that the concentration of carbonyl groups at the carbon surface is relatively high. This led the authors (124) to propose a donor-acceptor complex formation involving carbonyl-like oxygen and the aromatic ring of the phenol. Therefore, increasing activation temperatures up to 500°C increases the concentration of carbonyl groups at the surface. Further increase in activation temperature decreases this concentration.

For series 2, the first two bands corresponding to two adjacent carboxyl groups were not well defined. This indicated, probably, that activation with CO_2 suppressed the formation of carboxylic groups. The same observation was also true for carbonyl groups. These carbons showed lower capacities for adsorption of paranitrophenol.

For both series, the bands observed at 1620-1690 cm^{-1} and 1140-1230 cm^{-1} were weak. Interpretation of these bands was left for further investigation.

The study was further expanded to the case of non-graphitic carbonaceous surfaces (125). X-ray photoelectron spectroscopy (XPS) and IRS were used to study the type of bonding formed between oxygen and carbons prepared from polyvinylidene chloride (PVDC), polyfurfuryl alcohol (PFA), and cellulose. Some carbons were activated in CO_2 to different levels of burn-off (1, 32, and 67%). Atomic oxygen was used to react with carbons at room temperature for eight hours. The extent of surface complex formation amounted to about 50% of surface coverage. At the end of the adsorption runs, desorption of surface oxygen complexes was performed by heating the samples at $0.5^\circ\text{C}/\text{min}$ up to 800°C . Weight of samples during adsorption or desorption was monitored via a microbalance. A mass spectrometer served to analyze the desorption products.

For the unactivated PVDC heated up to 1300°C prior to adsorption, only one strong band (IRS) was obtained at 1725 cm^{-1} . This was attributed to a carbonyl group. For the carbon activated in CO_2 just to a 1% level of burn-off, two strong IRS bands appeared at 1630 cm^{-1} (enolic form; 1, 3 diketone) and at 1140 cm^{-1} (C-O bond). The carbon activated to a 67% level of burn-off showed three "very" strong bands at 1720 cm^{-1} (carbonyl or carboxyl), 1630 cm^{-1} (enolic) and at 1165 cm^{-1} (C-O bond). The sample activated to a 32% level of burn-off had characteristic bands of mixed states between the latter two samples.

Desorption data were referred to as integral thermal stability profiles (ITSP) and differential thermal stability profiles (DTSP). The former are plots of total weight of desorbed products per gram of original carbon versus desorption temperature. A DTSP is simply the derivative form of ITSP plotted versus desorption temperature. For all

carbons studied (125), the ITSP's showed a continuous variation of weight loss versus desorption temperature. Contrary to graphitic carbons, a plot of this behavior did not show linearity. With paracrystalline carbons (for example, PVDC), the continuity in ITSP is attributed to the existence of a large spectrum of reaction sites within the surface.

The DTSP's showed an increase in desorption rate up to a given temperature ($T_{\max}$); whereafter, the desorption rate decreased with increasing temperature. It was noted that increasing heat treatment temperature (HTT) prior to adsorption or activating the sample to higher levels of burn-off had a remarkable effect towards shifting $T_{\max}$ to higher values. The authors concluded (119), therefore, that the carbon-oxygen complex formed during adsorption was more stable for samples that had seen higher HTT or had been more activated with CO_2 . This may be discussed in terms of selective removal of structural components within the carbons during gasification by CO_2 . The less ordered structural components of the carbon are preferentially removed.

The effect of ion-bombardment on single-crystal surfaces of diamond or graphite was also studied by XPS (126). The surfaces were rather unreactive to molecular oxygen, only a fraction of the monolayer equivalent of oxygen was adsorbed. On the other hand, when the oxygen was excited by a microwave discharge prior to reaction with carbons, several oxygen layers were chemisorbed. The rate of adsorption was the same for diamond and graphite. Yet, the binding energy at the peak maximum (XPS output) for the $\text{O } 1s$ electron on diamond was 0.55 eV less than graphite. Furthermore, for both carbons, the width of the $\text{O } 1s$ signal was much greater than that of the $\text{C } 1s$ peak. The results indicated the

presence of at least two chemically distinct carbon-oxygen functional groups. The measured binding energy difference (0.55 eV) suggested the presence of differing proportions of the same two chemical species on the two carbons. For both C 1s and O 1s peaks, the peak areas were measured. After prolonged oxidation (high surface coverage), the ratio of these areas suggested an overall stoichiometry of $\text{CO}_{2.0} \pm 0.4$.

Identification of the two functional groups involved in the reaction was attempted by comparison with some reported data on several organic compounds (aliphatic aldehydes, ketones, acids, esters, and ethers). In the light of this study, the authors concluded (126) that for both carbons approximately half of the oxygen is present in ketonic groups ($\text{>C} = \text{O}$) and half in etheric linkages (C-O-C) on all oxidized surfaces.

Electrochemical investigations of surface functional groups on carbons have also been reported. For example, for an oxidized activated carbon, Frumkin (87) proposed that the surface oxide behaved as an oxygen electrode. Thus, in acid solution, the reaction was represented by

where $\text{C}_x \text{O}_x$ is a basic (referred to alkaline) surface oxide.

Garten and Weiss (90) proposed a different mechanism to explain the phenomenon of acid adsorption on activated sugar carbons. This is represented by

More recently, Boehm and Voll (127) concluded that none of the previous theories were entirely satisfactory. For the same phenomenon

of acid adsorption, they suggested the quinone-hydroquinone-type of complexes to exist at the carbon surface. The reaction was represented by:

In fact, the latter type of compounds was further confirmed (108, 128, 129). Polarographic studies (simply they are current-voltage relations) on an isotropic pyrolytic carbon electrode showed two distinct reproducible surface functionalities (129). These were attributed to an oxidized and a reduced state. Electrochemical transformation (usually achieved by changing the potential of the dropping mercury electrode to more positive or negative values) from one form to another or vice versa was shown to be quantitative. For example, at a given value of the applied voltage, the oxidized forms no longer existed at the surface, instead they were all in the reduced form. These groups could, in turn, be completely reoxidized at another range of voltage. The cycle was quantitatively repeated several times.

The specific adsorption of p-nitrophenol on both surfaces was also examined (129). The amount of p-nitrophenol adsorbed at the oxidized surface was substantially greater than that for the reduced form, thus indicating again that such quinone groups are responsible for specific adsorption of aromatic electron accepting compounds.

Surface acidity of carbon blacks has, more recently, been interpreted in terms of work function (130). The purpose of the study was to explore how various chemisorbed species influenced the surface potential of carbons. Measurements of contact potential difference were used to determine the work function. Further, the particles of

each carbon were brought into an aqueous slurry where the pH was measured. Unoxidized carbons were slightly basic (pH ~ 8), while oxidized carbons were acidic (pH 2-5). The relation between log-work function and pH was linear, thus indicating that the higher the concentration of surface protons, the more was the work function. Likewise, a linearity was observed between the oxygen content of the carbons and their corresponding work functions. This suggests that non-oxygen containing groups that may be present on the surface have a minor influence on the surface potential. The authors (130) suggested that the increase in work function with surface acidity could be interpreted to development of a space charge region as a result of charge exchange between chemisorbed oxygen species and free charge carriers in the crystallites of carbons. Thus, oxygen chemisorption could be viewed as affecting the electron affinity of crystallites via formation of a surface dipole layer.

2.2 CALORIMETRY--BRIEF REVIEW

A calorimeter is usually known as an instrument used to measure the heat involved in a known change in a state of material. This may include a change in phase, temperature, pressure, volume, chemical composition, or any other property of the material which is associated with the change in heat.

2.2.1 Types of Calorimeters

Calorimeters may be classified into several types. One method of classification is based on which physical variables are kept constant. The isothermal calorimeter is simply a heat flow calorimeter that operates at a given constant temperature. The most popular isothermal calorimeters are those used when a solid-liquid phase change or a

liquid-vapor phase change is taking place. The adiabatic calorimeter, on the other hand, has no heat transfer across its boundary. In fact, no practical adiabatic calorimeter exists. Even those named as adiabatic shielded calorimeters, which have external shields (or jackets) kept at the same operating temperature as that of the calorimeter, still have small heat leaks.

Sometimes a type of calorimeter is named after the scientist who first used it. Still the calorimeter could be isothermal or adiabatic. Examples of these calorimeters are the Bunsen ice calorimeter (operates at the melting point of ice), the Nernst calorimeter, the Calvet calorimeter, and the Joule twin calorimeter system. The latter model uses two calorimeters differentially to minimize errors due to heat leak. Frequently this calorimeter is known as the twin or differential calorimeter. The Dewar low-temperature calorimeter is of historical interest.

According to the ICTA, differential scanning calorimetry (DSC) denotes the technique which records the energy necessary to establish zero temperature difference between a substance and a reference material against either time or temperature as the two specimens are subjected to an identical temperature regime in an environment heated or cooled under controlled rates. The output thermogram represents the amount of heat supplied per unit time (131). However, the conventional terminology of DSC is generally practiced by recording the differential temperature versus time. This is actually defined as quantitative DTA (Differential Thermal Analysis) (132, 133). Recently, a DuPont DSC has been characterized as a technique whose output curve is directly proportional to the differential heat flow between a sample

and a reference material (5). The term "scanning" implies that the temperature of both the sample and reference is increased during the experiment at a known heating rate (5).

2.2.1.1 Low Temperature Adiabatic Calorimeters

Among this type of calorimeter, a series of relatively simple adsorption calorimeters were developed by Beebe and colleagues (134-139). The original model was a vacuum-jacketed metal calorimeter vessel into which adsorbate gas was admitted through a thin platinum tube. The vessel was suspended inside a glass jacket that was immersed in a constant temperature bath. The measurements of heat of adsorption required recording of temperature readings of the vessel as a function of time before and after admission of the gas. The heat capacities of the adsorbent and the calorimeter vessel were not measured directly but were estimated from the known weights. This model was later modified (140) by introducing a means for electrical calibration and better thermal shielding. In brief, the measurements of heat of adsorption were simply made by recording the variation of the temperature difference, ΔT , between the sample container and an outside bath (via a thermocouple junction) as a function of time. This value of ΔT combined with corrections for loss of heat by conduction and radiation was estimated to be proportional to the heat evolved during adsorption.

2.2.1.2 High Temperature Adiabatic Calorimeters

The most common adiabatic calorimeter used for adsorption studies (gases on solids) is the Beeck type calorimeter (141). This calorimeter was used by Brennan et al. (69, 142) and Klemperer and Stone (143) to study the heat of adsorption of gases on several evaporated metal films. In brief, the calorimeter consists of a very thin walled glass tube

wound with Pt wire which acted as a resistance thermometer. The tube was mounted vertically within an outer jacket through which a rapid stream of cold water was passed while the film was being evaporated on to the inner wall of the calorimeter tube. The tube was evacuated to avoid collapse during breaking and to reduce heat losses during measurements.

Gale et al. (144) used an adiabatic adsorption calorimeter for their study on granulated catalysts. Essentially it consisted of two concentric glass tubes joined at the bottom by a Dewar seal and mounted inside a jacket which was evacuated to 10^{-6} Torr. The concentric glass tubes were thin walled, and the annular space between the tubes was about 1 mm wide. On the outside wall of the outer tube was introduced fine gage nickel wire coils having a high electrical resistance. One of these coils served as a resistance thermometer, while the other was used for calorific determination. The assembly was mounted vertically and was totally immersed in water inside a large Dewar vessel. This calorimeter was sufficiently sensitive to measure heat liberation in the range of a few millicalories.

2.2.1.3 Isothermal Calorimeters

Isothermal calorimeters have also been used to measure the heat of adsorption at different temperatures (54, 145). Such calorimeters were used by Sevenster (54) to measure the heat liberated during the interaction between oxygen and some South African coals in the temperature range 0-80°C. The calorimeters operate at the melting of a specific calorimetric substance, a substance of very high purity such as ice (at 0°C) or phenol (at 41°C) or naphthalene (at 80°C). The calorimeter was brought to the desired conditions, that is, part of the substance

is solid and part molten. Briefly, a slight change in the sample temperature due to adsorption is compensated for via the calorimetric substance. Therefore, the solid/molten ratio will change according to the type of reaction under consideration. By observing a drift in the height of mercury placed in a fine capillary above the substance, the heat of adsorption is estimated.

2.2.2 Differential Scanning Calorimetry (DSC)

It appears that Mahajan et al. (5, 6) were the first to use the DSC technique to study the thermal effects involved during the pyrolysis (5) and hydrogasification (6) of coals. The results of thermal changes involved during the pyrolysis of twelve U.S. coals in a He atmosphere at 800 psi and up to 580°C were reported (5). Pyrolysis of coals having carbon contents in the range 78.8-91.2% (daf) was found to be endothermic in nature over the entire temperature range. However, for coals having carbon contents in the range 63.3-75.6%, pyrolysis showed endothermic and exothermic peaks. The net heat of the overall pyrolysis was either endothermic or exothermic depending on the carbon content. For coals having carbon contents less than 75%, the net heat was exothermic. The authors (5) concluded that previous DTA data were in error since no account for weight changes had been considered. Under rather similar experimental conditions, the DSC technique was used to study heats of hydrogasification of twenty coals (6). For all coals studied, this heat was exothermic and increased in magnitude with decreasing percentage carbon content (daf) in the coal.

2.3 CARBON-OXYGEN REACTION

As indicated earlier, the first step involved the gasification of carbon by oxygen is chemisorption of oxygen on the carbon surface (146).

Following this step, the gasification step occurs when CO and/or CO₂ are liberated in the gas phase. It is possible that one of the gasified products is once more chemisorbed at the surface, then oxidized, and finally gasified to a higher oxide state. A few of the possible reactions between carbon and oxygen can be represented by:

That is, at least thirteen reactions can take place when a carbon is exposed to oxygen. Equations 2.20, 2.21, 2.27, 2.28, and 2.30 are those representing adsorption. Gasification of chemisorbed species are given by 2.22, 2.24, 2.25, and 2.32. Also, gasification may occur when a chemisorbed species reacts with the oxidant 2.23, 2.31, or with the carbon matrix 2.26. Direct gasification via carbon-oxygen interaction or carbon-CO₂ interaction (equation 2.29) is unlikely to occur. It is difficult, therefore, to have a complete understanding on the

carbon-oxygen reaction since different carbons can possibly exhibit the inclusion of the above reactions to a greater or lesser degree.

A partial understanding of the carbon-oxygen reaction may be achieved through the following studies:

- (1) Chemisorption and physisorption of oxygen, CO, and CO₂ on carbon surfaces.
- (2) Carbon-CO reactions.
- (3) Carbon-CO₂ reactions.
- (4) Reactions of carbon complexes with O₂, CO, or CO₂.

In Section 2.1, a partial review of the first area was given. Areas (2) and (3) were thoroughly reviewed by Walker et al. (146).

In addition to the four above areas, it should be emphasized that during the course of one of the thirteen possible carbon-oxygen reactions, the nature of the surface may change. For example, when gasification occurs, more active sites are created. These sites may favor another reaction. In addition, during chemisorption, active sites are covered with oxygen. Since many of the C-O₂ reactions are exothermic, the local heat liberated may possibly remove some sites via annealing, that is, surface rearrangement. If the surface is exposed to a gas at given conditions and then at other conditions, and finally to the first conditions once more, it might show a totally different behavior. Thus, the history of the sample may, as well, affect the reaction. Unlike simple cases of metal-gas reactions, carbon reactions are rather complicated. In spite of this fact, there is evidence in the literature showing some regularities.

2.3.1 Mechanisms

Total agreement has been reached that CO and CO₂ are the primary products of the oxidation of carbons. The primary CO/CO₂ ratio

increases with increasing reaction temperature (23, 34, 147-156).

This ratio may depend on the type of carbon used (147) and the partial pressure of oxygen (147, 148, 22, 157).

2.3.2 Order of Reaction

Most of the work cited in the literature indicates that the carbon-oxygen reaction is first order (147, 149, 150, 158-162) in oxygen pressure. However, at oxygen pressures below 1.5 Torr, the reaction was found to be zero order (163, 164). Other authors (155, 157) had found the reaction to be half order.

2.3.3 Activation Energy for Gasification

Activation energies for interaction of oxygen with carbon (gasification) are reported to vary between 17 kcal/mole (149) to 110 kcal/mole (166). However, a value of about 50-60 kcal/mole is commonly reported in the literature (150, 162, 166). It is believed that the activation energy for the carbon-oxygen reaction depends on the type of carbon used, the surface coverage, and reaction temperature. If diffusional resistance of oxygen into the pore system is significant, the general observation is a lowering in the value of E_a . This is more pronounced at higher temperatures (146).

Dollimore et al. (166) have shown that for a PVDC carbon, the relation between E_d for desorption and θ was linear. At complete coverage ($\theta = 1$), values of E_d were scattered around 40 ± 5 kcal/mole. At zero coverage, these values were in the range of 85-110 kcal/mole depending on oxygen pressure. The effect of pressure on the value of E_d is more pronounced at low coverages. Increase of pressure affects the value of E_d in an irregular manner.

3. STATEMENT OF PROBLEM

The strength of an adsorption bond is reflected in the magnitude of the heat of adsorption. For the interaction between a carbonaceous material and oxygen, three major processes may occur; physical adsorption, chemisorption of oxygen at the surface, and gasification of carbon. The higher the heat of chemisorption, the stronger is the bond. Knowledge of the magnitude of heats of chemisorption of reactants, intermediates, and possibly, the gasified products elucidates the nature of gasification reactions.

When this work was initiated, the purpose was essentially to investigate some of the thermal effects involved during chemisorption of oxygen on chars and coals, that is, to determine the values of ΔH . For example, it is generally accepted that a known value of ΔH sheds more light on the mechanism of the reaction under consideration. Because of the lack of information about this subject matter in the case of carbonaceous materials, exploratory experiments had to be made on some commercial carbons and Saran chars whose reactivities towards oxygen chemisorption had previously been determined by thermogravimetric techniques. This was the first purpose of the work. For these carbons, the weight of oxygen uptake and of heat liberated versus reaction time, under somewhat analogous experimental conditions, were similar. That is, a sample chemisorbing more oxygen was found to liberate more heat (cal/g C) and vice versa.

At that stage, it was realized that a thermogravimetric technique was needed to determine the weights of oxygen uptake under conditions simulating those used for determination of the thermal effects. Since none of the commercial TGA units was helpful to serve this particular

demand, a home-made unit had to be built and then calibrated. This was the second purpose of this study.

With two particular Saran char samples, although gravimetric work showed a major difference in weight increase with time, thermal measurements showed that the heat liberated (cal/g C) was very close. With two commercial carbons, the amount of oxygen uptake was exactly the same. However, they liberated different amounts of heat. An up-to-date literature survey showed that little, if any, information is available on the thermal effects involved during oxygen chemisorption on carbons. As a consequence, it was reasonable to expand the study of these thermal effects on one or two Saran samples and to have a closer look at some of the experimental factors that could affect the measured value of heat liberated. Thereafter, the objectives of the present investigation were formulated. These were:

1. To explore a few factors that might play a role in determining the magnitude of heat of oxygen chemisorption. For example:

- (a) heating rate and desorption time and temperature during pretreatment,
- (b) reaction temperature,
- (c) flow rate of the oxidant and partial pressure of oxygen in the flow, and
- (d) particle size and bed height of the char.

2. To select a few of the important parameters mentioned above and to restudy them with the gravimetric technique.

3. To use the data obtained from 1 and 2 to calculate values of ΔH (kcal/mole), thus throwing some light on the nature of the bonds (or groups) formed between a specific char and oxygen during chemisorption.

4. To extend the study to the case of coal chars. This stage was not reached since the phenomenon of oxygen chemisorption on Saran chars proved to be more complicated, and yet more interesting, than had originally been anticipated. A firm base needed to be built before undertaking objective 4.

4. EXPERIMENTAL MATERIALS, APPARATUS,

AND PROCEDURE

4.1 SAMPLES

4.1.1 Unactivated Saran

Saran 498, supplied by the Dow Chemical Company, was used as the precursor for preparing the carbon in this study. Saran is a copolymer of vinylidene chloride and vinyl chloride in an approximate mole ratio of 90:10. A 25 lb batch was slowly heated to 900°C and held at this temperature for 4 hr in a flowing dry, high purity N₂ stream. Under these conditions, chlorine is liberated stoichiometrically as HCl, leading to the production of a microporous char (167, 168).

The char was ground and sieved into 35 x 60, 60 x 80, 80 x 120, 150 x 250, 270 x 325, and 325 x 400 mesh size fractions. Grinding was done either in an electric grinder having stainless steel gears or manually in a quartz lab mortar. Samples ground in the electric grinder were found to be contaminated with iron.

For most size fractions, iron as an impurity was determined in the following manner. Approximately 200 mg of the sample were heated in a muffle furnace at 5°C/min up to 900°C. The sample was then held at this temperature for 2 hr. The residual ash was dissolved in 10:1 mixture of HF and HClO₄. The resulting solution was evaporated to dryness. The final residue was dissolved in about 9N HCl. Iron was then determined colorimetrically by the orthophenanthroline method (169). The blank solution used for the determination was prepared by evaporating the same HF and HClO₄ mixture (used to dissolve the residue) to dryness; whereafter, perchloric acid was added and again the solution was evaporated. The final product was then dissolved in about 9N HCl.

Iron contents for various samples are listed in Tables 1 and

2.

TABLE 1

SAMPLE IDENTIFICATION AND IRON CONTENT FOR
SARAN CRUSHED IN ELECTRIC GRINDER

Sample Identification	Particle Size (mesh)	Iron Content (ppm)
Original Batch	--	23 - 26
S ₁ Fe	35 x 60	810
S ₂ Fe	60 x 80	516
S ₃ Fe	80 x 120	112
S ₄ Fe	150 x 250	101 - 104
S ₅ Fe	270 x 325	147 - 148
S ₆ Fe	325 x 400	200 - 205

TABLE 2

SAMPLE IDENTIFICATION AND IRON CONTENT FOR
HAND-CRUSHED SARAN CHARs

Sample Identification	Particle Size (mesh)	Iron Content (ppm)
S ₁	35 x 60	22
S ₂	60 x 80	19
S ₃	80 x 150	22 - 26
S ₄	150 x 250	14 - 22
S ₅	-250	25

4.1.2 Activated Saran

An activated sample of Saran char was available from a previous study (170). The following procedure had been used for activating the sample. A silica glass fluid bed reactor, 50 mm o.d. and 80 mm long, was used to conduct the activation of the S_4 Saran sample in one atmosphere of air at 425°C. The sample was first dried at 105°C prior to activation. Approximately 25 g were introduced into the preheated reactor under a flowing stream of N_2 and allowed to reach reaction temperature prior to introducing air. Following activation for 10 hr, the sample was cooled in N_2 . The activated sample, that is, S_{act} , was then reweighed. Weight loss due to gasification, referred to as the carbon burn-off, was found to be 63.8%.

4.1.3 Characterization of Saran Chars

Since most of the work described in this report was done on three samples, namely S_4 , S_4Fe , and S_{act} , it was reasonable only to characterize these chars. This includes determination of surface areas and mercury densities.

4.1.3.1 N_2 and CO_2 Surface Areas

A standard volumetric adsorption apparatus was used to measure N_2 uptake at -196°C and CO_2 uptake at 25°C. In brief, a known weight of the sample was outgassed overnight at 110°C until the pressure in the system was reduced to 10^{-4} Torr. Prior to studying the adsorption of either gas, free space measurements were made by using high purity helium. For each adsorption point throughout the study, an equilibrium time of 30-120 min was allowed. The volume of gas adsorbed (N_2 or CO_2) was calculated by using the ideal gas law.

In the case of N₂ surface area, data points were plotted according to the Brunauer-Emmett-Teller (BET) equation (171):

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C} \cdot \frac{P}{P_0} \quad 4.1$$

where P = adsorption equilibrium pressure, torr; P_0 = saturation vapor pressure of N₂, torr; and V = cumulative volume of N₂ adsorbed, cm³.

In general, the plot of $P/V(P_0 - P)$ versus P/P_0 is linear, provided $0.05 < P/P_0 < 0.35$. The monolayer volume of N₂, V_m , which covers the available carbon surface could, therefore, be calculated from the slope and intercept of the straight line. However, Saran is a microporous carbon; and, therefore, the range of validity of the BET equation does not extend to relative pressures of 0.35. In fact the BET plots for these carbons begin to depart from linearity when (P/P_0) exceeds 0.08. The range of relative pressures over which the BET plots were linear was 0.001-0.078. Similar observations are found in the literature (172, 173) for N₂ adsorption at -196°C on thermal carbon black graphitized at 3100°C. Therefore, with this narrow range of (P/P_0) , reproducibility of the experimental points obtained with Saran chars was poor; and, thus, N₂ surface areas calculated by the BET equation are uncertain.

An alternative method for determination of N₂ areas for porous materials is to use the plots of V versus P/P_0 . These are shown in Figure 2 for the three Saran chars. The plots display a rather long straight portion at relative pressures > 0.12 . The point at which the linear portion begins is known as "point B" (174). This point is taken to indicate the completion of the monolayer. In this connection, it has also been suggested that "point A," the point where the extrapolated linear branch cuts the adsorption axis (cf. Figure 2), may

Figure 2. Adsorption Isotherms for N_2 at $-196^\circ C$

represent the monolayer capacity. Apparently, there is no firm rule to decisively state whether the BET equation or either point "A" or "B" indicates the completion of the monolayer. Accordingly, three different values of N_2 surface areas, corresponding to the three different approaches, are given for each sample in Table 3. For this calculation, a cross-sectional area of $16.2 \text{ \AA}^2$ for a N_2 molecule was used (171, 174).

The CO_2 surface area at 25°C was calculated according to the Polanyi-Dubinin equation (175):

$$\log V = \log V_0 - 0.434 (BT^2/\beta^2)[\log (P_0/P)]^2 \quad 4.2$$

where V = amount of CO_2 adsorbed on the sample at equilibrium
pressure P , cm^3

V_0 = micropore volume, cm^3 .

P_0 = saturation vapor pressure of adsorbate (CO_2) Torr

β = affinity coefficient of adsorbate relative to benzene

The plot of $\log V$ versus $[\log (P_0/P)]^2$ gives a straight line with an intercept equal to $\log V_0$. Assuming V_0 to be equivalent to V_m and a value of $25.3 \text{ \AA}^2$ for the cross-sectional area of a CO_2 molecule (176), CO_2 surface areas were calculated. They are also presented in Table 3.

4.1.3.2 Active Surface Area

The active surface area, that is, the area occupied by carbon atoms located at the edges of basal planes and other defects, was determined by a conventional volumetric adsorption apparatus attached to a mass-spectrometer. A known weight of the sample, 0.3-1.0 g, was evacuated at room temperature until the pressure of the system dropped to 10^{-9} Torr. The sample was then heated at a rate of $20^\circ\text{C}/\text{min}$ up to 950°C , whereafter it was held for 48 hr. During the first few hours

TABLE 3
CHARACTERIZATION OF SARAN CHARS

Sample	N ₂ Area (m ² /g C)			CO ₂ Area (m ² /g C)	ASA (m ² /g C)	Mercury Density (g/cc)
	BET	Point "A"	Point "B"			
S ₄	808	826	848	1156	37	1.27
S ₄ Fe	901	948	961	1170-1190	--	1.15
S _{act}	1140	1283	1309	1210-1250	52	0.94

of the hold period, the decomposition products (CO and CO₂) increased the pressure to 10⁻¹ Torr, after which it dropped slowly to 10⁻⁷ Torr and then remained constant for 24 hr. Following this outgassing, the sample was cooled under vacuum to 100°C and oxygen was introduced at 1 atmosphere. The oxygen was allowed to react with the carbon for 48 hr, followed by evacuation of the system at 100°C until the residual pressure decreased to 10⁻⁸ Torr. The temperature of the sample was then raised stepwise to 950°C to desorb the chemisorbed oxygen. A liquid N₂ trap was used to freeze out the evolved CO₂. At the end of the experiment, the reactor was isolated from the system and the pressure of CO in the system was monitored using a Baratron gage. Afterwards, the liquid N₂ trap was removed, and the total pressure of CO and CO₂ in the system was measured. From the total amounts of CO and CO₂ evolved, the amount of oxygen chemisorbed at the carbon surface was calculated. For calculating the active surface area (ASA), a value of 8.3 Å² was assigned as the average area occupied by one oxygen atom chemisorbed on one carbon site of the surface (34). Values of ASA are given in Table 3.

4.1.3.3 Mercury Density

Mercury densities of the chars were determined by displacement of mercury while using an Aminco Laboratory Porosimeter (177). Briefly, a known weight of about 1.0 g of the sample was oven dried at 105°C for 30 min and then placed in a penetrometer of predetermined weight (a glass reservoir with a capillary stem graduated in divisions of 0.002 cc). The penetrometer, in turn, was inserted into a glass filling device and evacuated overnight to less than 50 microns pressure. Mercury was then introduced by tilting the glass filling device until the tip of the penetrometer was about 0.5 cm within the mercury pool.

By carefully opening a stopcock to the atmosphere, air was admitted until ambient pressure was reached. The penetrometer was removed, weighed, and transferred to a high pressure vessel. By applying the pressure on the mercury-filled penetrometer, the volume of mercury forced into the voids between the carbon particles was determined at 60 psi. It is noteworthy that above 60 psi, mercury penetration was almost negligible. Knowing the internal volume of the empty penetrometer, V_p , and the density of mercury at the filling temperature, d_{Hg} , the displacement volume of the sample, V_s , was calculated from

$$V_s = V_p - \frac{(W_p + W_s + W_{Hg}) - (W_p + W_s)}{d_{Hg}} - \Delta V_{Hg} \quad 4.3$$

where W_p , W_s , and W_{Hg} are the weights of the empty penetrometer, the sample, and the filling mercury respectively, and ΔV_{Hg} is deviation from complete filling. The apparent density of the sample, i.e., the mercury density, was calculated from the ratio of its weight to the displacement volume (178). Values of mercury density of the Saran chars are also given in Table 3.

4.2 ANALYSIS OF SAMPLE CONTAINERS

Three different types of sample containers were used for the present work. These were aluminum or gold pans supplied by the manufacturer and Vycor pans specifically designed to serve a particular purpose. Because of the high sensitivities of both techniques used in this report, analysis of the materials of these containers was required to help in the interpretation of some experimental results. To serve this purpose, each container was brought into solution for a subsequent determination of Fe, Co, Ni, Cu, Pb, Mn, and Ag as impurities. Aluminum containers were first dissolved in dilute HCl and evaporated to dryness. The resulting residue was dissolved in dilute HNO_3 , whereafter it was ready for analysis.

The Vycor pans were dissolved in a mixture of HF and HClO_4 (10:1) and evaporated to dryness. The final residue was dissolved in dilute HNO_3 .

The gold pans were dissolved in aqua regia and evaporated to dryness. However, when the resulting residue, chloroauric acid (HAuCl_4), was dissolved in dilute HNO_3 , it was reduced to spongy gold metal, i.e., a gold colloidal precipitate. At this stage, it was assumed that most of the foreign cations originally attached to the gold container remained in the mother solution. The filtrate of colloidal gold was, therefore, used for analysis.

A Perkin-Elmer 403 Atomic Absorption Spectrophotometer was used for determination of the cations mentioned above. For each cation determination, a series of standard solutions, having different known concentrations of this particular cation, were prepared. The unknown solution was analyzed against the whole series. For all cations

studied, no masking effect was observed. This was confirmed from atomic absorption results, where the concentration of each cation under consideration was almost the same and independent of the concentration of the standard series.

The concentration of impurities in the three sample containers are summarized in Table 4. It is noted that among these impurities, gold containers have the highest concentration of silver and copper. The possible significance of this will be commented on later.

TABLE 4
ANALYSES OF SAMPLE CONTAINERS

Element	Concentration of Impurity (ppm)		
	Aluminum Pans	Vycor Pans	Gold Pans
Fe	2500	150	240
Co	--	--	30
Ni	20	3	30
CU	100	10	200
Pb	50	--	40
Mn	30	10	10
Ag	100	--	500

4.3 GASES

Ultrahigh purity nitrogen was supplied by the Linde-Harvey Company. It is rated to have a minimum purity of 99.9999%, moisture content < 1 ppm, oxygen content < 1 ppm, CO and CO₂ < 0.3 ppm, and total hydrocarbons < 0.4 ppm. Dry grade oxygen or air was supplied by a local distributor (Philip Wolf Company, State College, PA). These gases had a minimum purity of 99.997% and a maximum moisture content of 3 ppm.

4.4 APPARATUS

4.4.1 DSC Apparatus

A DuPont DSC cell was used in conjunction with a cell base Module-II and a 990 Thermal Analyzer. The cell cross-sectional diagram is illustrated in Figure 3. The cell temperature is controlled by a silver heating block, a wound heater, and a platinum II control thermocouple. The cell makes use of a constantan disc as the primary means of heat transfer to or from the sample and reference positions and as one element of the temperature measuring thermoelectric junctions. A differential pair of chromel constantan thermocouples is provided by welding two chromel wires to the bottom centers of two raised platforms that support the sample and reference pans. Since the thermal resistance to the sample and reference pans is maintained constant, differential temperatures between the two pans are directly proportional to differential heat flow. The signal between these two junctions is fed to the cell base and, after amplification, monitored on the Y-axis of the 990 Analyzer. The sample platform has an additional welded alumel wire forming a chromel-alumel thermocouple junction. This drives the X-axis of the recorder with a signal indicating the sample temperature.

Gases are admitted to the sample chamber through an orifice in the block wall positioned midway between the two raised platforms. The gas is preheated by circulation through the silver block before entering the reaction chamber. The chamber silver lid has an opening to serve as a gas outlet. This design is recommended for flowing preheated gases to ensure excellent contact between the sample and the gas.

Figure 3. DSC Cell Cross-Section

The cell operates under reduced pressure down to 1 Torr or at ambient. In inert atmospheres, the cell can be heated up to 725°C; however, in the presence of an oxidant gas (O_2 or air), it is recommended not to operate the cell above 300°C.

The cell base Module II performs several functions. Basically, it serves as a differential heat amplifier as well as an electronic compensator for the sample and control thermocouples. It automatically selects the proper circuit to provide a particular linear heating rate. The cell base has a variable gain circuit which produces a constant calorimetric sensitivity at all temperatures for the DSC cell. A control knob located on the cell base maintains the base line at a horizontal position during experimental measurements.

The 990 Thermal Analyzer performs two basic functions: (i) it programs the cell to operate under chosen experimental conditions, and (ii) it records the output thermogram on chart paper. Further details of this unit are described elsewhere (179).

4.4.2 TGA Apparatus

None of the commercial TGA units was found to meet the experimental demands. Therefore, it was necessary to construct a TGA apparatus whose performance and accuracy match those obtained with the DSC apparatus. The major components of the TGA apparatus, shown in Figure 4, are:

1. A Cahn RG weighing mechanism placed in a glass vacuum bottle.
2. An electrobalance, i.e., a control unit for the weighing mechanism.
3. A Fisher 1-millivolt recorder to monitor weight changes, i.e., the output signal from the electrobalance.

Figure 4. Schematic Diagram for the TGA Apparatus

4. A vertical Vycor reactor attached to the vacuum bottle.
5. A furnace attached to a control unit and a thermocouple.
6. An auxiliary thermocouple connected to a potentiometer system with a sensitivity of 0.1 mV.

The weighing mechanism is a beam-type balance that works on the null principle. It has two ranges of sensitivity for maximum sample weight of 1.0 and 2.5 g, the range being determined by the choice of sample hook on the beam. For the present work, the more sensitive range was used. Prior to each run, the balance was calibrated and then electronically nulled following the manufacturer's specifications (180). A final adjustment was required so that the output recorder signal was a direct measure of weight change (one inch on the chart paper was equivalent to 10 or 20 μg).

At the top of the Vycor hangdown tube (16 mm I.D. and 90 cm long) there was located a stopcock attached to a flowmeter. This served as an inlet for the gases. Gases left the Vycor tube at the bottom and then passed through another flowmeter. This downflow for gases was found to substantially eliminate noise caused by aerodynamic forces inside the reactor. It might be mentioned that at elevated temperatures, a reactor having an I.D. greater than 16 mm caused a noise to the output signal. The larger the I.D. or the higher the temperature at which the reactor was operated, the more pronounced were aerodynamic forces. These forces introduced uncertainty in the balance readings, appearing to look like a wave characterized by peak to peak variation. Using the reactor described and operating at ambient pressure and a gas flow rate of 45 cc/min (N_2 , O_2 , or air), aerodynamic noise was found to be 2 μg at 100°C, 6 μg at 250°C, and 15 μg at 350°C. Further

explanation of these types of noise is considered in the literature (181-183).

A Vycor suspension wire (~ 0.5 mm O.D.) aligned inside the reactor was hooked to the balance beam. The sample container, which was a quartz bucket 1 cm o.d., 1 cm long, ~ 60 mg in weight, was hooked to the wire. At this stage, further adjustment was made so that the container was centrally located inside the reactor and about 1-2 mm above the tip of a thermocouple jacket attached to the reactor (cf. Figure 4). The thermocouple, inserted inside the jacket, was connected to a temperature control unit operating a locally made furnace. An auxiliary thermocouple was also inserted between the furnace wall and the reactor. At most temperatures used, the difference between the readings of the two thermocouples did not exceed $\pm 2^{\circ}\text{C}$.

4.5 CALIBRATION AND STANDARDIZATION

4.5.1 Calibration Coefficient (E) for DSC Cell

The value of the calibration coefficient E for the DSC cell was determined by two different methods. In the first method, a metal of high purity (indium, tin, or zinc) was used as a standard material. The cell was charged with an appropriate known weight of the metal. Nitrogen was passed at 45 cc/min; the cell was held isothermally for 20 min at 40°C below the melting point of the metal. It was then heated at $20^{\circ}\text{C}/\text{min}$ until melting of the metal was completed. The area A_f of the thermogram corresponding to melting was measured. Knowing the standard heat of fusion for the metal (Q_f), equation (4.4) was used to calculate the value of E. The results for these metals are summarized in Table 5.

TABLE 5

DETERMINATION OF THE CALIBRATION COEFFICIENT (E)
FOR DSC CELL BY USING STANDARD METALS

	Indium	Tin	Zinc
Q_f (cal/g)	6.79	14.14	27.05
Reported M.P. ($^{\circ}\text{C}$)	156.6	231.9	419.4
Observed M.P. ($^{\circ}\text{C}$)	157.0	232.0	419.0
Weight (mg)	2.88	1.15	1.02
B (min/in.)	0.05	0.2	0.1
Δq (mcal/sec/in.)	0.5	0.2	0.5
A_f (in. ²)	13.03	6.77	9.2
E (dimensionless)	1.000	1.001	0.999

In the second method used to determine the value of E, a sapphire disc, supplied by the manufacturer, was used. Two empty pans of the same weight were placed on the sample and reference platforms. Oxygen was passed through the apparatus at 45 cc/min. The cell was held isothermally at 80°C for 20 min and then heated at 20°C/min up to 300°C. This procedure was repeated under identical conditions with a weighed sapphire disc in the sample pan. The two scans are shown in Figure 5. Differences in the Y-axis deflection between the sapphire and the blank curves, ΔY , were measured at different temperatures. The values of the calibration coefficient E were calculated by using equation 4.5. Values of C_p for sapphire at different temperatures are available in the literature (184). Table 6 lists selected values of C_p and the corresponding values of E computed at different temperatures.

It can be concluded from Tables 5 and 6 that the value of E is independent of temperature or reaction atmosphere.

Figure 5. Determination of the Cell Calibration Coefficient Using Sapphire Disc

TABLE 6
VALUES OF (E) OBTAINED WITH SAPPHIRE DISC

Temp. (°C)	C _p (cal/g/°C)	ΔY (in.)	E
127	0.22545	4.80	0.999
157	0.23357	4.95	1.003
177	0.23835	5.05	1.003
207	0.24477	5.20	1.001
227	0.24860	5.30	0.998
257	0.25378	5.40	0.999
277	0.25690	5.45	1.002
307	0.26114	5.55	1.001

The values of E were also determined as a function of the carbon bed height. The two procedures mentioned above were also used. However, instead of placing the standard metal or the sapphire disc in an empty sample pan, a known weight of Saran carbon was placed first in the pan underneath the standard material. Values of E were determined as described earlier. The same procedure was repeated for several known weights of Saran carbon in a nitrogen atmosphere. In general, it was concluded that as the weight of the carbon bed (and, therefore, the height of the standard material from the bottom of the pan) increases, values of E increase. This behavior is shown in Figure 6. A similar trend was observed when other inter materials (Al₂O₃ or Graphon) were used in place of Saran char.

4.5.2 Calibration of TGA Apparatus

Two basic calibrations were required for the TGA apparatus: (i) the linearity of heating rate over a given temperature range, and (ii) the correct value of a particular temperature at the sample location

Figure 6. Variation of E with Original Saran Char Weight

compared to the observed temperature. Linearity of heating rate was manually adjusted by selecting the proper voltage used to heat the furnace element. A variac-transformer was used to serve this purpose. Thus, the trial-and-error method was followed prior to experiments.

In order to standardize the apparatus for accurate temperature measurement, preliminary tests were needed with standard materials. The decomposition temperatures, T_1 and T_2 , of calcium oxalate monohydrate were determined as a function of the heating rate as well as sample weight. Here T_1 and T_2 are defined as the decomposition temperatures for the reactions $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$ and $\text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3 + \text{CO}$, respectively.

Both DSC and TGA techniques were used for this study where different weights of the oxalate were heated at several rates in N_2 at 45 cc/min. The results obtained with the DSC technique are summarized in Table 7. It is observed that at a constant heating rate of $20^\circ\text{C}/\text{min}$, increase of the original weight of the oxalate shifts T_1 to higher values but does not affect the value of T_2 . On the other hand, when the weight of the sample is kept constant, an increase in heating rate is shown to increase both T_1 and T_2 , with the latter being ill-defined below $10^\circ\text{C}/\text{min}$.

With the TGA apparatus, only the effect of sample weight was studied at a fixed heating rate of $20^\circ\text{C}/\text{min}$. Results are shown in Table 8. It is seen that although the value of T_1 increases regularly with sample weight, T_2 does not follow a regular pattern. However, with the TGA apparatus values of T_2 are scattered around an average of 422°C . Several trials were made in an attempt to correlate values of T_1 and T_2 obtained with the DSC apparatus with those recorded by TGA;

TABLE 7
DECOMPOSITION TEMPERATURES OF
CALCIUM OXALATE MONOHYDRATE--DSC TECHNIQUE

Starting Weight (mg)	Heating Rate (°C/min)	Decomposition Temperature (°C)	
		T ₁	T ₂
1.5	20.0	107	ill-defined
3.0	20.0	117	455
6.5	20.0	123	455
10.0	20.0	128	456
13.6	20.0	135	457
18.0	20.0	141	457
10.0	0.5	95	ill-defined
10.0	1.0	100	ill-defined
10.0	2.0	106	ill-defined
10.0	5.0	114	ill-defined
10.0	10.0	121	444
10.0	20.0	128	456

however, no firm conclusion was drawn. Therefore, a few standard metals and alloys were thereafter used for temperature calibration of the TGA apparatus.

It is known that the melting temperatures of these materials are not affected by either heating rate or sample weight. Lead, zinc, aluminum, and two different alloys, referred to as solders A and B in this text, were used. Melting points of these solids were determined using both the DSC and TGA apparatus. In the case of the TGA, a strip of the metal was hooked to the hangdown Vycor wire via a rhenium wire. The distance of suspension between the middle of the strop and the tip of the thermocouple-jacket was kept constant at 1-2 mm.

TABLE 8
DECOMPOSITION TEMPERATURES OF
CALCIUM OXALATE MONOHYDRATE--TGA TECHNIQUE

Starting Weight (mg)	Decomposition Temperature (°C)	
	T _i	T ₂
0.6	90	403
3.0	90	404
5.0	109	402
7.5	116	436
25.0	136	428
47.0	150	434
86.0	162	430
119.0	178	424
150.0	191	432

The reactor was heated at given experimental conditions until the melting point of the standard material was reached. This was detected when the material melted, dropping off the hook, and thus indicating a sudden weight change in the TGA output signal. The comparative values of melting temperatures obtained with both apparatus are listed in Table 9. The plot of DSC transition temperatures versus those read on the TGA indicator gage is shown in Figure 7. In the temperature range 180-660°C, a straight line is observed. Extrapolation to 0°C on the TGA temperature axis corresponded to 35°C on the DSC axis. Evidently, the TGA temperature indicator gage was reading 35°C below the actual temperature of the sample under consideration since the readings of the auxiliary thermocouple were almost 35°C higher than the gage.

TABLE 9
MELTING TEMPERATURES OF METALS AND ALLOYS

Material	Melting Temperature (°C)		
	True	DSC	TGA (Indicator Gage)
Solder A	--	183	145
		184	145
Solder B	--	231	195
		231	194
Solder C	--	179	145
		179	145
Lead	327.4	280*	240
Zinc	419.5	420	375
		419	385
Aluminum	660.0	660	590
		660	600
		660	585

*Evidently, the lead used for this calibration was contaminated with some other impurities. This explains the major difference between the true value of melting point and that determined by the DSC technique.

4.6 WORKING EQUATIONS

4.6.1 DSC

For a given thermal change occurring inside the DSC cell, the amount of heat Q released or gained by the material is given by

$$Q = \frac{A}{m} (60 \times B \times E \times \Delta q) \quad 4.4$$

where Q = heat of the reaction (cal/g material)

A = area of the thermogram (in.²)

m = weight of sample (mg)

E = cell calibration coefficient (dimensionless)

B = time base setting of the recorder (min/in.)

Δq = Y-axis range of the recorder (mcal/sec/in.)

Figure 7. Relationship between DSC Temperature and That Recorded by TGA Control Thermocouple

When a sapphire disc was used to calculate the value of E, the following equation was used:

$$E = \left(\frac{C_p}{\Delta Y} \right)_T \times \left(\frac{H_r \times m}{60 \times \Delta q} \right) \quad 4.5$$

where C_p = heat capacity of sapphire at a given temperature (cal/g/°C)

ΔY = displacement in Y-axis at the same temperature (in.)

H_r = heating rate = 20°C/min

m = weight of sapphire = 63.8 mg

Δq = Y-axis range = 1.0 cal/sec/in.

4.6.2 TGA

Simple arithmetic was used to calculate weight changes recorded by the TGA apparatus. No working equation was used.

4.7 SENSITIVITY AND PRECISION

4.7.1 DSC

The calorimetric sensitivity of the system is 2 μ cal/sec. The precision of the DSC output is reported to be $\pm 1\%$.

4.7.2 TGA

The sensitivity of the Cahn balance is 2 μ g/in. The precision of the system was found to be $\pm 3\%$.

4.8 OPERATING PROCEDURE

The operating procedure used with both apparatus was basically the same. In the case of DSC, a known weight of sample (usually 10-12 mg) was placed in the proper pan (aluminum, gold, or Vycor). The pan was placed on the sample platform inside the cell. The cell was locked in place and then flushed with UHP-N₂ at 45 cc/min. In the case of TGA, a known sample weight (between 50-100 mg) was placed in a quartz bucket and then suspended inside the reactor. The reactor was attached to the vacuum bottle and then flushed with UHP-N₂ at 45 cc/min.

DSC cell or TGA reactor was outgassed down to 1 Torr for 15 min and then flushed with N_2 using the same flow rate. The sample was heated at $20^\circ\text{C}/\text{min}$ from ambient temperature to 600°C (unless otherwise mentioned), held at this temperature for 30 min, and then cooled to room temperature. This pretreatment took about 4 hr with the DSC cell and about 10 hr with the TGA reactor (the TGA apparatus required longer time to reach room temperature).

Thereafter, the sample was heated isothermally for 30 min in N_2 at a chosen reaction temperature in the range $75\text{--}300^\circ\text{C}$. At the end of this period, the oxidant gas (oxygen or air) was introduced over the sample to replace N_2 at the same flow rate. With the DSC apparatus, the scan was started and the output thermogram was recorded for 28 min reaction time. With the TGA apparatus, weight changes were monitored as a function of time for a period of 0.5–48 hr, depending on the information wanted.

4.9 CALCULATIONS

4.9.1 Values of Q (cal/g C)

With the DSC technique, a typical thermogram with a hypothetical base line is illustrated in Figure 8(a) for the reaction between a Saran char and an oxidant gas. Line ab represents part of the base line when the char is held isothermally in N_2 . At b, the oxidant is introduced to replace N_2 . When this takes place, 2 min are required for the oxidant to reach the carbon (point c). Once the exothermic reaction starts at c, the experimental scan cei is recorded. With the DSC technique, it is known that if the experimental scan is located above the base line, the reaction is exothermic. On the other hand, for an endothermic reaction, for example, melting of a metal, the thermogram is recorded below the base line. The exothermicity of the

Figure 8. Typical DSC Data for Char-Oxygen Interaction at an Isothermal Temperature

Saran-oxygen interaction was further confirmed by the following procedure. At selected intermediate points (f, g, and h), N_2 was allowed to replace the oxidant. For all points, the scan dropped down to and continued along the base line. This indicates that the area above the base line is a direct measure of the heat released for the carbon-oxygen interaction. It was noted at point i (attained after 28 min reaction time) that deviation between the scan and the base line was not large enough to obtain reliable data. Therefore, DSC runs were terminated by this time. For each thermogram, the area was divided into small segments, ΔA , corresponding to several time intervals, Δt . The total Area, A , scanned at a given reaction time, t , was then calculated by adding values of ΔA . This gave the integral area responsible for the reaction. Equation 4.4 was then used to calculate the integral heat released, Q (cal/gC), at selected reaction times. The plot of Q versus t is shown in Figure 8(b).

4.9.2 Values of W (mg Oxygen/g C)

The TGA output curve is almost similar to the Q - t plot shown in Figure 8(b). Thus, the integral weight, W (mg oxygen/g C) was directly recorded on the chart paper of the TGA apparatus. The sensitivity of weighing was such that meaningful data could be obtained over much longer times than was the case in the DSC apparatus. In some cases, when it was desired to calculate values of fractional surface coverage, TGA runs were recorded for 48 hr.

4.9.3 Values of ΔH (kcal/mole)

For the interaction between oxygen and Saran chars, values of ΔH (kcal/mole) for chemisorption were calculated by:

$$(\Delta H)_{T,t} = \left(\frac{Q}{W_+} \right)_{T,t} \cdot 32 \quad 4.6$$

where Q = heat evolved at given experimental conditions

W_+ = weight of oxygen chemisorbed

T = reaction temperature

t = reaction time

4.9.4 Fractional Surface Coverage (θ)

Long term TGA runs were made at 100°C to calculate fractional surface coverage θ for the first 28 min reaction time. The sample was exposed to oxygen until essentially saturation equilibrium conditions were reached. That is, the active surface area was completely covered with oxygen; and, therefore, no further increase in the weight was detected. This was confirmed by constancy of output signal from the balance to the recorder. If W_+ is the weight of oxygen chemisorbed, measured or calculated (cf. equation 6.4) at reaction time t, W_{tot} is the total oxygen taken up by the sample in the TGA to reach saturation conditions, and W_{ASA} is the weight of oxygen uptake (as measured in the adsorption apparatus-mass spectrometer combination) used to calculate active surface area (ASA) accessible to oxygen, then the fractional surface coverage θ is

$$\theta = (W_{ASA} - W_{tot} + W_+) / W_{ASA} \quad 4.7$$

Equation 4.7 was used to calculate values of θ .

5. RESULTS

5.1 CHARACTERIZATION OF CARBONS

Studies in this report were initiated by using three commercial carbons, namely: Barneby-Cheney, Westvaco, and Columbia. For these samples, reactivity towards oxygen chemisorption at 140°C had previously been measured using thermogravimetric studies (170). The results are shown in Figure 9. The carbons used, as supplied by the manufacturer but dried at 110°C prior to each run, are referred to as (DRY) samples. In some cases, the samples were also washed with an HCl-HF mixture to remove inorganic impurities. These are referred to as demineralized (DEM) samples. According to the previous findings (170), when either the Barneby-Cheney or the Columbia carbon was demineralized, the amount of oxygen uptake was lowered. For the Westvaco carbon, however, both (DRY) and (DEM) samples had the same amount of oxygen uptake at 140°C.

In the present study, the DSC technique was used to characterize the same carbons at 140°C following the conventional pretreatment procedure mentioned earlier (Section 4.8). The Q-t plots are shown in Figure 10. It is noted that at a given time interval, the higher the amount of oxygen uptake (Figure 9), the higher is the value of heat released (Figure 10). In the case of Westvaco samples, a better resolution was obtained with the DSC technique. Thus, the (DRY) carbon released slightly higher values of Q as a function of time than did the (DEM) sample.

At this stage, it was concluded that the DSC technique would be useful to characterize carbons in terms of their reactivities towards oxygen chemisorption. Therefore, three Saran chars (particle size 150 x 250 mesh) were further considered. Using both DSC and TGA

Figure 9. Chemisorption of Oxygen on Commercial Activated Carbons at 140°C

Figure 10. Heat of Chemisorption of Oxygen on Commercial Activated Carbons at 140 °C

techniques and following the conventional pretreatment procedure (Section 4.8), Saran chars were exposed to oxygen at 100°C. Figure 11 shows the variation of the amounts of oxygen uptake (dotted lines) and the values of heat released (solid lines) with reaction time. The activated Saran chemisorbs more oxygen and, thus, releases more heat than the other two carbons. On the other hand, the unactivated Saran (S_4) has the lowest levels of W-t and Q-t plots. For the S_4Fe sample, that is, the unactivated Saran which was contaminated with iron (101 ppm) as an impurity during grinding, the position of either the W-t or the Q-t plot is almost mid-way between the S_{act} and the S_4 samples.

For the Saran chars, values of ΔH at 100°C (computed by using equation 4.6) were independent of reaction time. These values are 75 ± 2 , 68 ± 2 , and 42 ± 1 kcal/mole oxygen chemisorbed on the S_{act} , S_4Fe , and S_4 samples, respectively.

For reasons to be given later in Section 6, values of ΔH may not be used for characterization of carbons. Instead, values of Q , measured under identical pretreatment and reaction conditions, are more meaningful for the sake of comparison.

5.2 EFFECT OF PRETREATMENT PARAMETERS ON THE HEATS OF SARAN CARBON-OXYGEN INTERACTION

5.2.1 Purity of Nitrogen

In an earlier stage of this study, purified N_2 was used. However, while facing some technical difficulties, it was advisable to use ultrahigh pure (UHP) N_2 . These difficulties arose when the internal bright disc of the DSC cell changed to a dark color at the end of each run. As a consequence of this observation, it was not certain whether the value of the calibration coefficient, E , was constant throughout the

Figure 11. Values of Q (cal/g C) and W (mg/g C) at 100°C for Saran Chars

run, or whether it was changing (gradually while the cell was heated to 600°C) during the pretreatment procedure. When UHP-N₂ was used, there was no observed change in the color of the disc prior to and after the run. Accordingly, UHP-N₂ was used in the present work.

Considerations were given to understand the above phenomenon. It was concluded that the value of E was changing before and after each pretreatment procedure. Furthermore, for the oxygen chemisorption step, the value of E remained constant. Apparently with purified N₂ (which had an oxygen content of ~ 5-8 ppm), the material of the disc was oxidized at or around 600°C. This oxidation step did not occur below 300°C (reaction temperature).

Similar to the oxidation of the cell-disc, Saran chars were believed to react at 600°C with O₂ as an impurity in the flowing N₂. To explore this effect, two similar runs were made at 281°C on the S₄ sample. In the first run, the carbon was pretreated with purified N₂ and then reacted with oxygen at the above temperature. The proper correction for the value of E was made. In the second run, UHP-N₂ was used in place of purified N₂. No correction for the value of E was required. Values of Q obtained for both runs at 281°C are given in Table 10. With purified N₂, values of Q are higher than those obtained with UHP-N₂. This indicates that during preheat treatment with purified N₂, the carbon may have been activated (oxidized) to a certain (but unknown) level of burn-off. As the nature of the carbon surface changes, more pores are opened, increased amounts of oxygen uptake are observed, and, therefore, higher amounts of heat are liberated.

5.2.2 Heating Rate

The effect of heating Saran chars in N₂ at different rates ranging between 1 and 100°C/min prior to their exposure to oxygen was studied.

TABLE 10

DEPENDENCE OF Q AT 281°C ON PURITY OF N₂
USED DURING PRETREATMENT--S₄ SAMPLE

Reaction Time (min)	Q (cal/g C)	
	Purified N ₂ *	UHP-N ₂ **
2	6.79	4.92
4	9.70	7.37
6	11.76	9.18
8	13.44	10.71
10	14.86	12.03
12	16.10	13.18
15	17.76	14.75
20	20.11	16.96
25	22.01	18.77
28	23.09	19.74

* Oxygen content 5-8 ppm
** Oxygen content < 1 ppm

During the conventional pretreatment procedure, the sample was heated at a desired rate (1, 2, 5, 10, 20, 50, or 100°C/min) to 600°C, held at this limit for 30 min, and finally cooled in N₂ to room temperature. Values of Q at 100 and 202°C were measured for the S_{act} and the S₄ samples, respectively. Table 11 lists these cumulative values of Q at 28 min reaction time. It is evident that: (i) for lower heating rates (below 5°C/min), values of Q increase with increasing heating rate, and (ii) values of Q are independent of heating rate above 10°C/min.

TABLE 11
EFFECT OF HEATING RATE DURING PRETREATMENT ON Q
AFTER 28 MINUTES REACTION TIME

Sample	Reaction Temperature (°C)	Q (cal/g C)						
		Heating Rate (°C/min)						
		1	2	5	10	20	50	100
S ₄ Fe	202	4.71	5.04	5.78	5.89	5.65	5.59	5.73
S _{act}	100	2.32	2.89	3.05	3.66	3.84	3.63	3.68

5.2.3 Desorption (Heat Treatment) Temperature

It is generally accepted that the amount of oxygen chemisorbed at a carbon surface is dependent on desorption temperature, T_{des} , that is, the temperature which the sample had been subjected to during heat treatment prior to oxygen chemisorption. In general, higher T_{des} are known to remove more carbon-oxygen complexes from the surface. As a result, more active sites accessible to oxygen chemisorption would be expected to be generated.

5.2.3.1 Values of Q (cal/g C)

With the DSC technique, and aluminum pans used as sample containers (melting point of aluminum=660°C), the maximum T_{des} is limited to 600°C. It is reasonable, therefore, to use gold or Vycor pans instead of aluminum. These containers could be heated to higher temperatures before melting. However, the maximum operating temperature of the DSC cell is reported to be 720°C. Therefore, the effect of T_{des} on the subsequent chemisorption reaction at 100°C was limited to the temperature range 450-700°C.

The first step was to explore how reproducible the results were with the use of either gold or aluminum pans under identical experimental conditions. The S_{act} sample was exposed to oxygen at 100°C.

For T_{des} of 500°C, values of Q_{Au} measured with gold pans were higher than those obtained with aluminum pans, Q_{Al} . The same observation was true for a T_{des} of 600°C. The term A_T is introduced here as

$$A_T = (Q_{Au}/Q_{Al})_T \quad 5.1$$

Values of A_{500} and A_{600} were dependent on reaction time (cf. Table 12) but independent of T_{des} . The average values of A_T , A_{ave} , decrease with increasing reaction time (Column 4, Table 12). For T_{des} at 700°C, the experimental values of Q_{Au} (Column 5) were divided by the corresponding values of A_{ave} to yield the calculated values of Q_{Al} (Column 6), that is, the values of Q which would have been measured experimentally if aluminum pans were used. Column 7 reports the experimental values of Q_{700} determined with Vycor pans. It is seen that these values are in reasonable agreement with those given in Column 6.

A further study was made using Vycor pans for T_{des} of 500 and 600°C. In both cases, a given value of Q_{Vycor} was almost comparable with that obtained with the aluminum pan at the same time interval and reaction temperature. This probably indicates that the decrease in the value of A_{ave} with increasing reaction time is due to a catalytic effect of gold on the chemisorption reaction of oxygen on the Saran chars.

The dependence of Q at 100°C (for the S_{act} sample) on desorption temperature, T_{des} , during pretreatment is illustrated in Figure 12. For a given time interval, increase in T_{des} increased the subsequent value of Q for oxygen chemisorption.

TABLE 12
CALCULATED VALUES OF Q_{Al} AT 100°C FOR T_{des} AT 700°C

1	2	3	4	5	6	7
t (min)	A_{500}	A_{600}	A_{ave}	(Q_{Au})	$(Q_{Al})_{700}^*$	Q_{Vycor}^{**}
2	1.46	1.49	1.475	2.44	1.65	1.90
4	1.41	1.42	1.415	3.43	2.43	2.69
6	1.39	1.37	1.380	4.11	2.98	3.22
8	1.37	1.34	1.355	4.65	3.43	3.62
10	1.34	1.34	1.340	5.10	3.81	3.96
12	1.33	1.30	1.315	5.50	4.19	4.25
15	1.32	1.28	1.300	6.02	4.63	4.64
20	1.29	1.26	1.275	6.72	5.27	5.17
25	1.27	1.25	1.260	7.35	5.83	5.62
28	1.26	1.25	1.255	7.64	6.08	5.86

* Calculated values
** Experimental values

5.2.3.2 Values of ΔH (kcal/mole)

A similar study was made with the TGA unit to investigate the effect of T_{des} on the amount of oxygen uptake at 100°C on the S_{act} sample. Since with the TGA unit, Vycor containers have been used throughout the whole study, no catalytic effect of sample container on the chemisorption reaction needed to be considered.

As a secondary objective of this work, it was reasonable to explore the dependence of ΔH on values of fractional surface coverage θ . Therefore, TGA runs were recorded for a period of 48 hr. By this time, further increase in sample weight due to oxygen uptake was negligible. These long time TGA runs were required to determine the total amount of

Figure 12. Dependence of Q at 100°C on Desorption Temperature and Sample Container-- S_{ac} Sample

oxygen uptake on the samples. Equation 4.7 was then used to calculate appropriate values of θ .

The data listed in Table 13 show the dependence of weight of oxygen uptake at 100°C on T_{des} . It is seen that increase in T_{des} (prior to chemisorption) from 450-700°C increases the weight of oxygen uptake at the same time interval. This information is similar to that illustrated in Figure 12 for the dependence of Q on T_{des} .

The computed values of ΔH are given in Table 14. Here, for each desorption temperature, the values of ΔH are generally independent of reaction time. In some cases, the value of ΔH computed at 2 min reaction time is slightly different than the mean value obtained for other time intervals. This could be attributed to differences in time required for oxygen to replace N_2 in the DSC cell and the TGA unit. Therefore, for each desorption temperature, an average value of ΔH was computed. The values of $(\Delta H)_{\text{ave}}$ seem to be identical for T_{des} at 450 and 500°C. However, increase in T_{des} from 500 to 700°C increases $(\Delta H)_{\text{ave}}$.

Since the range of θ varied between 0.64 and 0.86 for T_{des} at 700 and 450°C, respectively, it was interesting to further consider lower values of θ . As mentioned earlier, the maximum operating temperature for the DSC cell is limited to 700°C. The following experiment was then performed. The TGA quartz reactor was used to heat 100 mg of the sample in N_2 at 20°C/min up to 950°C. The sample was held at this temperature for 30 min and then cooled to room temperature. This treatment was believed to more completely clean the carbon surface via more desorption of CO and CO_2 . The calculated values of θ for this run (see below) confirm this assumption. At the end of this treatment, part of the sample was rapidly transferred to the DSC cell and the

TABLE 13

DEPENDENCE OF W (mg oxygen/g C) AT 100°C ON T_{des}

Reaction Time (min)	W (mg oxygen/g C)				
	T_{des} (°C)				
	450	500	550	600	700
10	0.802	0.912	0.942	1.001	1.547
15	0.942	1.094	1.131	1.194	1.781
25	1.197	1.351	1.420	1.561	2.131

TABLE 14

DEPENDENCE OF ΔH (kcal/mole) AT 100°C ON
 T_{des} AND SURFACE COVERAGE (θ)

Reaction Time (min)	T_{des} (°C)									
	450		500		550		600		700	
	θ	ΔH	θ	ΔH	θ	ΔH	θ	ΔH	θ	ΔH
2	0.81	61	0.72	55	0.70	67	0.68	79	0.64	85
10	0.83	59	0.75	58	0.73	66	0.71	77	0.70	78
20	0.85	61	0.77	60	0.75	67	0.73	76	0.72	82
28	0.86	61	0.78	61	0.77	66	0.75	76	0.74	80
$(\Delta H)_{\text{ave}}$	60 ± 2		58 ± 3		66 ± 1		77 ± 2		81 ± 3	

remainder was used for a TGA run. Once more, in each apparatus, the sample was desorbed in N_2 at $600^\circ C$ using the regular procedure. Values of Q (cal/g C) and W (mg oxygen/g C) were then determined at $100^\circ C$. The computed values of θ varied between 0.46 and 0.56 for time intervals between 2 and 28 min. Values of ΔH scattered around a constant value of 80 ± 3 kcal/mole. This value is similar to that obtained following T_{des} at $700^\circ C$ (cf. Table 14), even though the coverage range over which chemisorption occurred was significantly lower than that following desorption at $700^\circ C$. Figure 13 summarizes the effect of heat treatment temperature on values of ΔH for oxygen chemisorption at $100^\circ C$.

5.2.4 Desorption (Soak) Time, t_{des}

The effect of desorption time, t_{des} , at T_{des} of 600 or $700^\circ C$ prior to oxygen chemisorption at $100^\circ C$ was studied on the S_{act} sample. During the regular heat treatment procedure, the sample was heated in N_2 at $20^\circ C/min$ up to 600 or $700^\circ C$. The sample was held at each T_{des} for a period of time ranging between zero and 10 hr. The regular procedure was thereafter followed to measure the values of Q or W .

5.2.4.1 Values of Q (cal/g C)

The results in Figure 14 show the dependence of Q at $100^\circ C$ on soak time at $600^\circ C$. For this set of experiments, aluminum pans were used as sample containers. It is evident that increase in t_{des} from zero to 5 hr during desorption decreases the subsequent values of Q for oxygen chemisorption. This could possibly be due to deactivation of the sites accessible to oxygen during the desorption step (annealing). Apparently, for desorption times longer than 5 hr, there is no

Figure 13. Dependence of ΔH at 100°C on Desorption Temperature-- S_{act} Sample

Figure 14. Dependence of Q at 100 °C on Desorption Time at 600 °C Prior to Oxygen Chemisorption-- S_{act} Sample

significant additional effect. Thus, curve V in Figure 14 is the same for t_{des} of 5 and 10 hr.

Similar results were found at T_{des} of 700°C (gold pans). However, at t_{des} greater than 10 min, no significant effect on Q was detected. For the sake of comparison, Table 15 has been constructed. An arbitrary reaction time of 25 min (in oxygen) has been chosen. For each T_{des} , the value of Q obtained at the longest t_{des} was taken as unity. Other values of Q obtained for shorter t_{des} were then normalized to the chosen value.

It is noted that the effect of deactivating the sites is more accelerated at the higher T_{des} (700°C). Thus, for T_{des} of 700°C, no significant change in the values of Q was detected at t_{des} greater than 10 min. For T_{des} of 600°C, the same conclusion was true for t_{des} greater than 90 min.

5.2.4.2 Values of ΔH (kcal/mole)

The effect of desorption time at 600°C prior to oxygen chemisorption at 100°C was also studied using the TGA technique. Typical W vs t plots are shown in Figure 15. The trend is similar to that shown in Figure 14. Thus, increase of t_{des} at 600°C from zero to 5 hr was found to decrease the subsequent weight of chemisorbed oxygen at 100°C. For t_{des} longer than 5 hr, the effect is insignificant.

Values of ΔH (kcal/mole) at 100°C calculated for different desorption time intervals are given in Table 16. Since for each single run, these values were independent of chemisorption time, only those selected at 10, 15, and 25 min are reported here. It is noted from the table that a constant value of $\Delta H = 76 \pm 2$ kcal/mole is obtained

TABLE 15

NORMALIZED VALUES OF Q^* AT 25 MIN REACTION TIME FOR
DIFFERENT DESORPTION TIMES AT 600 AND 700°C

Desorption Temperature (°C)	Desorption Time (min)						
	None	5	10	30	90	300	600
600 (aluminum pans)	1.71	1.53	--	1.42	1.08	0.99	1.00
700 (gold pans)	1.14	1.08	1.02	1.00	--	1.00	--

*S_{act} Sample--reaction temperature: 100°C

TABLE 16

VALUES OF ΔH^* (kcal/mole) AT 100°C
CALCULATED FOR DIFFERENT DESORPTION
TIME INTERVALS AT 600°C

Chemisorption Time (min)	Desorption Time (min)				
	None	5	30	90	300
10	77	77	77	77	77
15	77	76	76	76	78
25	75	76	76	76	77

*S_{act} Sample

Figure 15. Dependence of Weight of Oxygen Chemisorbed at 100 °C on Desorption Time at 600 °C-- S_{act} Sample

in all cases. This value is neither dependent on desorption time at 600°C nor on chemisorption time at 100°C.

It is also noted from Tables 15 and 16, and Figures 14 and 15 that although desorption time at 600°C affects both values of Q (cal/g C) and W (mg/ g C), it does not affect the values of ΔH (kcal/ mole).

This interesting observation led to further examination of the total increase in weight of oxygen uptake at 100°C as a function of time when the S_{act} sample was subjected to some selected heat treatment conditions at 600°C. The TGA unit continued to record weight changes for a period of 20-25 hr. Results for three different runs are shown in Figure 16. For the first run (curve I), the sample was treated in the conventional manner, that is, kept at 600°C for 30 min. In the second run (curve II), the pretreatment conditions were similar to the first run, however, the sample was kept at 600°C for 5 hr. The sample used for the third run (curve III) was first heated in N_2 at 30°C/min up to 950°C, and then held at this temperature for 30 min. After the sample was cooled to room temperature, it was transferred to the TGA unit where, once more it was subjected to the regular heat treatment conditions (600°C for 30 min).

As mentioned earlier, for the first 30 min reaction time, the weight of oxygen chemisorbed following pretreatment II was less than that chemisorbed following pretreatment I. This was true up to about 5 hr chemisorption time, at which period the two curves intersected. For reaction times greater than 5 hr, the two curves reversed their positions, thus curve II fell above curve I. Furthermore, for the sample which had been pretreated at 950°C, although it was subjected

Figure 16. Oxygen Uptake at 100°C for the S_{act} Sample Subjected to Different Heat Treatment Conditions at 600°C--Duplicate Runs Shown

to air during the transfer step, the oxygen uptake was higher at all times than that found following pretreatments I and II.

For the sake of confirmation, each of the previous three runs was repeated two to three times on fresh samples. In all cases, the data points were duplicated within 1-2% deviation.

5.2.5 Desorption-Adsorption Cycles

This study was devoted to investigate a possible dependence of ΔH on surface coverage θ . In a simple way, it was reasonable to subject a Saran sample to some selected pretreatment conditions prior to oxygen chemisorption at 100°C. For each run values of ΔH were computed for the first 28 min reaction time. Calculation of the corresponding values of θ required the TGA runs to extend for 48 hr.

In brief, a fresh S_{act} sample was (i) subjected to the regular pretreatment procedure up to a given T_{des} (500, 600, or 700°C), (ii) held at T_{des} for 30 min, and then cooled to room temperature, (iii) reacted with O_2 at 100°C until reaching the saturation conditions (48 hr), and (iv) cooled to room temperature. Steps (i)-(iii) and (iii)-(iv) are referred to as desorption and adsorption cycles, respectively. Following the first cycle, an identical procedure was performed on the same sample [steps (i)-(iv)]. This is designated here as the second cycle. Thereafter, a third desorption-adsorption cycle was performed on the same sample. Thus, for desorption temperatures of 500, 600, and 700°C, three successive cycles were conducted on the same sample.

With the DSC technique, values of Q for each cycle were recorded during the first 28 min reaction time. However, the sample was allowed to react with oxygen (at 100°C) for a period of 48 hr inside the cell.

The effect of desorption-adsorption cycles on values of Q and W is illustrated by the data listed in Table 17. For the sake of simplicity, selected values of Q or W are only presented here at a reaction time of 15 min. Similar trends were observed at other time intervals. It is noted that for each desorption temperature, a given value of Q for any cycle is lower than that found for the preceding but higher than that found for the subsequent cycle. In other words

$$Q_1 > Q_2 > Q_3 \quad 5.2$$

The same trend was observed for the values of W at a given reaction time.

$$W_1 > W_2 > W_3 \quad 5.3$$

Values of ΔH for the three cycles are given in Table 18. For a particular cycle and desorption temperature, an average value of ΔH , ΔH_{ave} , was observed. This phenomenon indicated that although the fractional surface coverage θ was changing by 3-15% (depending on the cycle and T_{des}), $(\Delta H)_{ave}$ remained almost constant. However, $(\Delta H)_{ave}$ was markedly affected by desorption temperature, as well as by the history of the sample. For T_{des} of 500°C, $(\Delta H)_{ave}$ for the three cycles was almost constant. For T_{des} of 600 or 700°C a sharp drop in the value of $(\Delta H)_{ave}$ for each successive cycle was seen. That is,

$$\Delta H_1 \geq \Delta H_2 > \Delta H_3 \quad 5.4$$

Apparently, heat treatment of Saran chars completely covered by chemisorbed oxygen may possibly regenerate a new surface having different sites than those originally existing on the fresh sample. Therefore, values of ΔH are more dependent on the history of the sample than on surface coverage.

TABLE 17

SELECTED VALUES OF Q (cal/g C) AND W (mg oxygen/g C)
FOR THE S_{act} SAMPLE SUBJECTED TO SUCCESSIVE DESORPTION-
ADSORPTION CYCLES--REACTION TIME: 15 MIN

T_{des} (°C)	Cycle					
	First		Second		Third	
	Q_1	W_1	Q_2	W_2	Q_3	W_3
500	2.00	1.094	1.22	0.684	0.88	0.501
600	3.25	1.354	2.00	1.026	1.18	0.650
700	4.43	1.781	2.39	1.473	1.37	1.091

TABLE 18

DEPENDENCE OF ΔH (kcal/mole) ON CYCLING

T_{des} (°C)	Cycle					
	First		Second		Third	
	θ_1	$(\Delta H_1)_{ave}$	θ_2	$(\Delta H_2)_{ave}$	θ_3	$(\Delta H_3)_{ave}$
500	0.72-0.78	58±3	0.79-0.84	58±3	0.87-0.90	56±3
600	0.68-0.75	77±2	0.73-0.80	65±3	0.82-0.87	58±2
700	0.64-0.74	81±4	0.68-0.77	51±3	0.71-0.77	42±4

5.3 EFFECT OF REACTION TEMPERATURE ON THE HEATS OF SARAN CHAR-OXYGEN INTERACTION

Dependence of Q and W on reaction temperature was investigated in the range 75-300°C for the three Saran chars. In all experiments mentioned in this section, the samples were subjected to the same conventional heat treatment procedure in N_2 (600°C for 30 min).

5.3.1 Values of Q (cal/g C)

For Saran samples, the genral trend of Q - t plots was essentially the same (cf. Figure 11) at different temperatures. Increase in reaction temperature shifted a particular Q - t curve to a higher position. Typical plots for the S_{act} sample are shown in Figure 17. Similar results were observed for the S_4 and S_4Fe chars. At a given time interval, the higher the reaction temperature, the greater was the amount of heat liberated. This behavior has been examined using the DSC technique up to 300°C.

The data in Figure 17 were used to construct Arrhenius plots. At three chosen time intervals, 10, 15, and 25 min, the rates of heat released R_t (where $R_t = Q/t$, and $t = 10, 15$, or 25 min) were calculated for each reaction temperature. The plots of R_t (cal/g C/min) versus reciprocal of absolute temperature ($1/T$) are shown in Figure 18 for the S_{act} sample. These plots are linear over a given range of temperature. For each R_t , two linearities are observed, the first linear region starts at 75°C and ends at 125°C. The second linearity is obeyed in the temperature region 125-202°C. The calculated activation energies for the first and second regions amounted to 4.7 and 7.2 kcal/mole, respectively. These values are independent of the reaction time at which the rates have been computed. It appears,

Figure 17. Dependence of Heat Released on Reaction Temperature and Time for Interaction between Oxygen and S_{act} Sample

Figure 18. Dependence of Rate of Heat Released on Reaction Temperature-- S_{act} Sample

therefore, that for the S_{act} sample, the kinetics of the carbon-oxygen interaction below 125°C is somehow different than that above 125°C.

With the other two Saran samples (S_4 and S_4Fe), a similar behavior was observed, that is, the Arrhenius plots were also discontinuous. For both samples, values of R_t at 100°C fall above the corresponding lines. This may suggest the existence of one more linear region which could extend to lower temperatures. Because of poor reproducibility of the DSC data at such low temperatures, runs at these temperatures are not reported. However, it was evident from the plots that a discontinuity appeared in the range 200-215°C. The calculated activation energies below 200°C amounted to 5.7 and 5.1 kcal/mole for the S_4 and S_4Fe samples, respectively. At higher temperatures (above 215°C), these values were 9.7 kcal/mole (S_4) and 8.7 kcal/mole (S_4Fe).

5.3.2 Values of ΔH (kcal/mole)

Using the TGA technique, weight changes at several reaction temperatures were monitored as a function of time. In all cases studied, a weight gain was recorded. For the S_4 and S_4Fe samples, increase in reaction temperature monotonically shifted the W-t plot to a higher weight gain as a function of time. For the S_{act} sample, however, this behavior (cf. Figure 19) was not strictly found. As reaction temperature increased from 75 to 177°C, the W-t plots showed a higher weight gain as a function of time. At 202°C, the net weight gained at any reaction time was lower than the corresponding gain at 177°C. In this regard, it is suggested that the net weight gain recorded by the TGA unit could, in fact, be the result of two simultaneous reactions taking place at the carbon surface. One is responsible for a weight

Figure 19. Dependence of Weight Gain on Reaction Temperature and Time for Interaction between Oxygen and S_{act} Sample

gain, W_+ , while the other is accompanied by a weight loss W_- . At a given moment, the net weight gain observed experimentally, W_{exp} , is given by:

$$W_{\text{exp}} = W_+ - W_- \quad 5.5$$

Evidently, both W_+ and W_- are dependent on reaction temperature. This will be shown shortly.

Values of ΔH were calculated in the manner described earlier in Section (4.9.3). For the S_{act} sample, only values at 75, 100, 125, 150 and 177°C are reported here. For the other two samples, ΔH between 100 and 227°C is considered. Table 19 and Figure 20 describe the dependence of ΔH on reaction time and temperature.

For each sample, values of ΔH at 100°C are independent of reaction time. The average values for the S_{act} , S_4 , and $S_4\text{Fe}$ samples are 77 ± 2 , 41 ± 1 , and 68 ± 1 kcal/mole, respectively. Values of ΔH at 125°C do not follow the same trend. The S_{act} sample has a value of ΔH comparable to that at 100°C. For the other two samples, the apparent values of ΔH increase sharply with reaction time. At temperatures above 125°C, all samples show the same behavior, that is, the apparent value of ΔH increases with reaction time at a given temperature or with reaction temperature at a given time. For example, for the S_4 sample, the spread in ΔH values increases with temperature from 43-56 kcal/mole at 125°C to 107-164 kcal/mole at 227°C (cf. Figure 21). This phenomenon is attributed to a gasification process taking place simultaneously with the chemisorption process. The latter was previously thought to be the only reaction occurring at a measurable rate at such low temperatures. According to the working equation ($\Delta H = 32 Q/W$) together with equation 5.5, an ideal chemisorption reaction

TABLE 19
VALUES OF ΔH (kcal/mole) FOR THE THREE CHAR SAMPLES

Reaction Time (min)	ΔH (kcal/mole)					
	100°C			125°C		
	S_{act}	S_4	S_4Fe	S_{act}	S_4	S_4Fe
2	79	42	69	75	43	80
10	77	41	68	76	50	83
20	77	41	69	76	54	86
25	76	42	68	76	56	88

(say at 100°C) leads to a constant value of ΔH which is independent of reaction time. This is only true when

$$W_{exp} = W_+ \quad 5.6$$

or

$$W_+ \gg W_- \quad 5.7$$

or

$$W_- \approx 0 \quad 5.8$$

As the temperature increases above 100°C, the weight increase due to oxygen uptake, W_+ , as well as the weight decrease due to carbon gasification, W_- , both increase. Obviously, the contribution of W_- to W_{exp} increases more rapidly with increasing temperature than does the increase of W_+ to W_{exp} . This is part of the explanation for the increase in ΔH values with increasing temperature and time. Added to this is the complexity in Q values. When gasification occurs at such "low" temperatures, it is not certain whether the gasified products are CO or CO₂ or even a mixture of CO and CO₂ (which could also vary with reaction temperature). In the rigorous case, a different value for the heat of reaction must be assigned to each individual step. However,

Figure 20. Dependence of ΔH (kcal/mole) on Reaction Temperature and Time

Figure 21. Variation of ΔH and W_p with Reaction Time for S_{act} Sample at $75^\circ C$

with the present experimental set-up, there is no feasible method to analyze the products. Some mathematical calculations and assumptions are presented shortly to clarify this argument (Section 5.3.4).

5.3.3 Physical Adsorption

For a reaction temperature of 75°C, the S_{act} sample showed a different behavior. Values of ΔH increased with reaction time (up to about 15 min) and finally attained a constant value of 67 kcal/mole (cf. plot I, Figure 21). This behavior suggested a possible simultaneous occurrence of both physical adsorption and chemisorption of oxygen at the carbon surface. Therefore, it was desirable to investigate the extent of physical adsorption on the S_{act} sample at 75°C in the manner described below. Following the regular pretreatment, the sample was first exposed to oxygen at 100°C for 48 hr, after which no additional weight increase was observed. The sample was then outgassed and finally flushed with N_2 at 75°C. Oxygen was once more introduced to replace N_2 at the same flow rate. Under these conditions, an increase in the sample weight W_p , was ascribed to physical adsorption of oxygen. The dependence of W_p (mg oxygen/g C) on reaction time was monitored for 28 min (plot II, Figure 21 and Table 20). For the first 15 min, values of W_p increased with time, thereafter W_p was almost constant.

If W_{exp} is the total weight of oxygen uptake due to physical adsorption and chemisorption, the amount of oxygen chemisorbed, W_+ (mg oxygen/g C) is given by:

$$W_+ = W_{exp} - W_p \quad 5.9$$

Equation 5.9 was used to compute values of W_+ . These were used to compute the corresponding values of ΔH for only oxygen chemisorption.

TABLE 20

PHYSICAL ADSORPTION AND CHEMISORPTION OF OXYGEN ON THE S_{act} SAMPLE AT 75°C

t	Q	W_{exp}	$\Delta H'$	W_p	W_+	ΔH
(min)	(cal/g C)	(mg O_2 /g C)	(kcal/mole)	(mg O_2 /g C)	(mg O_2 /g C)	(kcal/mole)
2	0.561	0.346	(51.9)	.089	0.257	69.9
4	0.935	0.519	(57.6)	.093	0.426	70.2
6	1.179	0.635	(59.4)	.096	0.539	70.0
8	1.384	0.727	(60.9)	.104	0.623	71.1
10	1.560	0.785	(63.6)	.107	0.678	73.6
12	1.717	0.855	(64.3)	.111	0.744	73.8
15	1.916	0.923	(66.4)	.114	0.809	75.8
20	2.178	1.028	(67.8)	.114	0.914	76.3
25	2.401	1.132	(67.8)	.114	1.018	75.5
28	2.518	1.189	(67.8)	.114	1.075	75.0

The results are listed in the last column of Table 20. Values of ΔH are computed from W_{exp} and Q , that is, before taking into consideration the additional weight of physically adsorbed oxygen.

It is noteworthy that the first four values of ΔH give an average value of 70.3 kcal/mole, while the last four values are scattered around 75.7 kcal/mole (also cf. plot III, Figure 21). The difference between the two, that is, 5.4 kcal/mole, may be considered as the heat of physical adsorption. This parameter, being small, cannot be directly determined using the DSC technique at 75°C because of the small amount of physical adsorption.

Experimental trials were made to measure the weight of oxygen physically adsorbed at 100°C. It was concluded that at this temperature or above, physical adsorption was negligible.

5.3.4 Calculation of the Weights Gasified

Consideration is given here to understanding the kinetics of gasification of the S_4 sample in the temperature range 125-227°C. Actual gasification runs were also made in the temperature range 450-850°C. These are illustrated in Section 5.5.

Four methods of calculation were followed. In each case, few assumptions were introduced. Subsequently, at a given temperature and reaction time, the weight of gasified products W_* (cf. equation 5.5), expressed as mg gasified/g C, was computed. The same calculations were made with the other two samples (S_{act} and $S_4\text{Fe}$). Since similar findings were reached, these data were omitted.

5.3.4.1 Method I

With this method, no correction was made to account for the contribution to Q from the gasification process. In other words, the value

of $\Delta H = 41$ kcal/mole was assumed to be the correct value between 125-227°C. The actual variation of the enthalpy term with reaction temperature was obviously neglected. The magnitude of this variation, which can be estimated from the variation in heat capacities of the reactants and products, is small compared to the experimental errors encountered in calculating values of ΔH reported in this report.

For the S₄ sample between 125-227°C, chemisorption of oxygen is given by:

$$(\Delta H)_{t,T} = 32 (Q/W_+)_{t,T} = 41 \text{ kcal/mole} \quad 5.10$$

The term W_+ represents the actual weight of oxygen chemisorbed (mg/g C) if gasification were not occurring. The experimental weight, W_{exp} , recorded by the TGA unit (cf. equation 5.5) expresses the difference in weight between W_+ and the weight of carbon gasified, W_- (mg/g C). Using equation 5.10 to compute values of W_+ and by knowing the corresponding values of W_{exp} , equation 5.5 was used to calculate W_- .

Attempts were made to study the dependence of W_- on reaction time or temperature. Evidently, the kinetics of gasification at such low temperatures do not follow a rigid rule. Log-log plots of W_- versus reaction time are shown in Figure 22. At 125°C, the relation between W_- and t is linear. At the highest two temperatures, linearity is almost observed between W_- and $\sqrt{t}$. For intermediate temperatures, the relation is a mixed state between the above two extremes.

The calculated rates of gasification at 10 and 20 min are listed in Table 21. Increase in reaction temperature increases the rate of carbon gasification.

Figure 22. Relation between Weight of Char Gasified for S_4 Sample and Reaction Time--Method I

TABLE 21
CALCULATED GASIFICATION RATES FOR THE S₄
SAMPLE--METHOD I

Temp. (°C)	Gasification Rate (mg/g C/min)	
	Reaction Time (min)	
	10	20
125	1.45×10^{-2}	1.45×10^{-2}
150	7.50×10^{-2}	6.75×10^{-2}
177	17.5×10^{-2}	14.5×10^{-2}
202	35.0×10^{-2}	27.0×10^{-2}
227	55.0×10^{-2}	36.0×10^{-2}

5.3.4.2 Methods II and III

In this case, attention was given to the contribution of the gasification reaction to the value of Q . When both gasification and chemisorption are occurring simultaneously, the value of heat measured experimentally, Q_{exp} (cal/g C), involves two terms, thus

$$Q_{\text{exp}} = Q_{\text{C}} + Q_{\text{g}} \quad 5.11$$

where Q_{C} and Q_{g} are the heats evolved during chemisorption and gasification, respectively. Since both reactions are exothermic, the negative signs on both sides of equation 5.11 are cancelled.

For a typical chemisorption reaction on the S₄ sample (that is, at 100°C), the value of ΔH is 41 kcal/mole. Assuming this value to be valid at higher reaction temperatures (125-227°C), equation 5.10 becomes

$$Q_{\text{C}} = \frac{41}{32} \times W_{+} \quad 5.12$$

where W_{+} and Q_{C} are respectively expressed as (mg oxygen/g C) and (cal/g C). Equations 5.5 and 5.12 give

$$Q_{\text{C}} = \frac{41}{32} (W_{\text{exp}} + W_{-}) \quad 5.13$$

When the carbon is gasified, the products are CO or CO₂ or a mixture of both. The heats of combustion of β -graphite are 27 kcal/mole and 95 kcal/mole for the formation of CO and CO₂, respectively. Assuming that for Saran carbons, these heats of combustion do not vary much and provided that the atomic weight of carbon is 12, one may introduce

$$Q_g = \frac{27}{12} W_- \quad (\text{formation of CO}) \quad 5.14$$

or

$$Q_g = \frac{94}{12} W_- \quad (\text{formation of CO}_2) \quad 5.15$$

Substituting equation 5.13 with either 5.14 or 5.15 in equation 5.11, one gets

$$W_- = 0.282 (Q_{\text{exp}} - 1.281 W_{\text{exp}}) \quad 5.16$$

or

$$W_- = 0.110 (Q_{\text{exp}} - 1.281 W_{\text{exp}}) \quad 5.17$$

Either equation 5.16 or 5.17 could be used to calculate the values of W_- (mg/g C). The choice depends upon whether the carbon is gasified to CO or CO₂. It can be realized that in either case, the kinetics of gasification are expected to follow the same pattern. For example, if at a given instant, R is the rate of gasification to form CO₂, then the term $(0.282R/0.110)$ is the rate of gasification to form CO at the same instant.

Equation 5.17 was used to calculate values of W_- (formation of CO₂) when the S₄ sample was exposed to oxygen in the temperature range 125-227°C. Similar to the observations seen when using method I, the plots of $\log W_-$ versus $\log t$ were linear (cf. Figure 23). Therefore,

Figure 23. Relation between Weight of Char Gasified for S_4 Sample and Reaction Time--Methods II and III

apart from the method used to calculate the values of W_- , the general trend is essentially the same. Thus,

$$W_- = A (t)^m \quad 5.18$$

where A is a constant (temperature dependent), and $1.08 \geq m \geq 0.55$.

The calculated gasification rates leading to CO and CO₂ formation are listed in Table 22.

TABLE 22
CALCULATED GASIFICATION RATES FOR THE
S₄ SAMPLE--METHODS II AND III

Temp. (°C)	Gasification Rate (mg/g C/min)			
	CO ₂ Formation		CO Formation	
	10 Min	20 Min	10 Min	20 Min
125	2.95×10^{-3}	2.00×10^{-3}	7.5×10^{-3}	5.3×10^{-3}
150	10.5×10^{-3}	7.5×10^{-3}	27.8×10^{-3}	19.5×10^{-3}
177	17.8×10^{-3}	13.7×10^{-3}	45.8×10^{-3}	35.5×10^{-3}
202	28.8×10^{-3}	18.4×10^{-3}	74.0×10^{-3}	47.9×10^{-3}
227	44.8×10^{-3}	32.8×10^{-3}	11.7×10^{-2}	85.4×10^{-3}

5.3.4.3 Method IV

When the carbon is gasified producing a mixture of CO and CO₂, the ratio of the concentrations of these produces is governed by (23)

$$(CO/CO_2) = A_{\text{exp}} (-64000/RT) \quad 5.19$$

where A is a constant, T is the absolute temperature, and R is the gas constant. Values of A ranging between 100 and 300 have been reported depending upon such variables as active site concentration on the carbon and the fraction of the active sites covered by oxygen-complex. In this study, A is assumed to equal 150. Following this approach, the ratios of CO/CO₂ are 0.045, 0.072, 0.114, 0.166, and 0.234 at 125, 150,

177, 202, and 227°C, respectively. Taking these ratios into consideration, values of ΔH for gasification amount to 93, 91.4, 88.9, 86.2, and 82.9 kcal/mole gasified. Substituting these values for ΔH in place of the "27" in equation 5.14 or "94" in equation 15 and following the same procedure of computation, one gets:

$$W_- = B (Q_{\text{exp}} - 1.281 W_{\text{exp}}) \quad 5.20$$

where B equals 0.111, 0.113, 0.115, 0.118, and 0.123 at 125, 150, 177, 202, and 227°C, respectively. Values of W_- were then calculated. Plots of $\log W_-$ versus $\log t$ are illustrated in Figure 24, while the rates of gasification are listed in Table 23. It is noted that the slopes of the lines in Figure 24 are similar to those in Figure 23.

TABLE 23

CALCULATED GASIFICATION RATES FOR THE S₄ SAMPLE--METHOD IV

Temp. (°C)	(CO/CO ₂)	Gasification Rate (mg/g C/min)	
		10 Min	20 Min
125	0.045	2.97×10^{-3}	2.10×10^{-3}
150	0.072	11.0×10^{-3}	7.7×10^{-3}
177	0.114	18.3×10^{-3}	14.3×10^{-3}
202	0.166	30.5×10^{-3}	19.7×10^{-3}
227	0.234	50.0×10^{-3}	36.6×10^{-3}

5.3.5 Dependence of the Calculated Gasification Rates on Temperature

The data listed in Tables 21-23 indicate little increase in gasification rates with temperature (compared to the results shown in Section 5.5.2). It is interesting to further understand the effect of temperature on the calculated gasification rates. Arrhenius plots (cf. Figure 25) were then made from the data listed at 10 min in

Figure 24. Relation between Weight of Char Gasified for S_4 Sample and Reaction Time--Method IV

Figure 25. Arrhenius Plots for Calculated Gasification Rates at 10 Minutes Reaction Time

these tables. It is not certain for any of the plots whether a break does exist between two linear regions, or whether log-rates vary asymptotically with reciprocal of temperatures. Evidently, at least, the value of activation energy for gasification is decreasing with increasing reaction temperature. Extrapolating these linear plots to $T = 100^{\circ}\text{C}$, gave an estimated gasification rate of 0.6 to 1.7×10^{-3} (mg/g C/min) depending on the method of calculations (I, II, III, and IV). Therefore, a weight of 6 to 17×10^{-3} mg/g C is expected to gasify at 10 min reaction time. This figure is much less than the weight of oxygen uptake (0.63 mg/g C - cf. Figure 11) measured at 100°C for a reaction time of 10 min. This confirms the assumption made in equation 5.7.

5.4 DEPENDENCE OF Q ON REACTION PARAMETERS

DSC studies were extended to investigate the effect of carbon bed height and particle size as well as the oxygen flow rate and partial pressure on the values of Q at a given reaction temperature.

5.4.1 Carbon Bed Height

In order to examine the existence of oxygen diffusional effects down through the carbon bed, two samples were considered: the S_4 at 281°C and the S_{act} sample at 100°C . The original weight of samples were varied between 5.0 and 19.5 mg. As mentioned earlier, for each sample weight, depending on the density and attractive forces between particles, a certain value of the calibration coefficient, E, had to be assigned. Previous considerations of this subject matter are explained in Section 4.5.1 and Figure 6.

Selected values of Q at four reaction intervals are given in Table 24 for the S_{act} sample and in Table 25 for the S_4 sample. The

TABLE 24

EFFECT OF CARBON BED HEIGHT ON
Q AT 100°C--S_{act} SAMPLE

Chemisorption Time (min)	Q (cal/g C)				
	Original Weight (mg)				
	6	11	14	15	19.5
10	2.32	2.31	2.47	2.44	2.51
15	2.84	2.94	2.86	2.86	2.92
20	3.21	3.33	3.27	3.29	3.31
28	3.81	3.87	3.89	3.86	3.98
E	0.992	1.061	1.083	1.089	1.124

TABLE 25

EFFECT OF CARBON BED HEIGHT ON
Q AT 281°C--S₄Fe SAMPLE

Reaction Time (min)	Q (cal/g C)			
	Original Weight (mg)			
	5	8	12	16
10	11.8	12.1	12.2	12.1
15	14.4	14.6	14.7	14.6
20	16.2	16.4	16.5	16.4
28	18.5	18.5	18.6	18.3
E	1.010	1.045	1.092	1.141

corresponding values of E are also included in the tables. It is seen that between 100-281°C, changing the original weight of the sample has essentially no effect on Q at a given reaction temperature and time. This observation is true whether the reaction involves only chemisorption (Table 24), or chemisorption and gasification (Table 25). It is concluded, therefore, that resistance to diffusion of oxygen down through the carbon bed does not limit either the rate of chemisorption or gasification.

5.4.2 Particle Size of Carbon

The dependence of Q at 281°C on particle size was earlier investigated on the unactivated samples (S_1Fe-S_6Fe series - cf. Table 1) which had been reduced in size in an electric grinder having stainless steel gears. Values of Q at two selected time intervals are given in Table 26. Decrease of particle size from 35 x 60 to 150 x 250 mesh was accompanied by a decrease in Q at comparable time intervals. When the samples were analyzed for iron, it was found that the iron content decreased with decrease in particle size of the carbon. This is taken as a direct indication of the catalytic activity of iron for carbon-oxygen interaction at 281°C.

Once more, the effect of particle size on Q had to be studied. Therefore, the original batch of Saran was crushed in a lab mortar and then sieved into different size fractions. Values of Q for the different samples (series S_1-S_5) were measured at 281°C. These values are listed in Table 27. It is evident that changing the particle size from 35 x 60 to the -250 fraction does not have any influence on Q at a reaction temperature of 281°C. Concurrently, the iron content in these samples is markedly reduced over that found in the samples.

TABLE 26

IRON CONTENT AND VALUES OF Q AT 281°C--S_nFe SAMPLES

Particle Size (mesh)	35x60	60x80	80x120	150x250	270x325	325x400
Identification	S ₁ Fe	S ₂ Fe	S ₃ Fe	S ₄ Fe	S ₅ Fe	S ₆ Fe
Fe Content (ppm)	810	516	112	101	152	202
Q at 2 Min	7.22	5.96	5.38	5.28	5.22	5.02
Q at 28 Min	29.9	21.0	20.5	19.7	19.7	19.5

TABLE 27

DEPENDENCE OF Q AT 281°C ON PARTICLE SIZE--S_n SAMPLES

Particle Size (mesh)	35x60	60x80	80x150	150x250	-250
Identification	S ₁	S ₂	S ₃	S ₄	S ₅
Fe Content (ppm)	18-27	--	22-26	14-22	--
Q at 2 Min	4.73	4.48	4.54	4.54	4.24
Q at 28 Min	16.7	16.7	16.7	16.7	16.6

prepared in the electric grinder. Further, the spread in concentration of iron in the samples has been reduced.

5.4.3 Oxidant Flow Rate

The effect of oxidant flow rate on Q was studied with air flowing over the S_4Fe sample at $281^\circ C$, as well as with oxygen passing over the S_{act} sample at $100^\circ C$. During the conventional heat treatment procedure, the flow rate of N_2 was not kept at 45 cc/min. Instead, it was adjusted at a particular lower rate in the range 9-45 cc/min. When the oxidant gas was passed over the sample to replace N_2 , care was taken to insure that both the rates of N_2 and the oxidant were identical. Values of Q were then measured. These are reported in Table 28.

It is observed that for a given temperature and time, values of Q are independent of the flow rate of oxidant. This is true whether the oxidant gas used is O_2 or air. Therefore, diffusional resistance of oxygen through the reaction chamber inside the DSC cell has negligible effect on the rate of oxygen chemisorption or gasification.

5.4.4 Partial Pressure of Oxygen

For this study, the S_{act} , the S_4Fe , and the S_4 samples were used at reaction temperatures of $100^\circ C$ or $227^\circ C$. The work was oriented to: (i) explore a possible relation between Q measured at given experimental conditions and the partial pressure of oxygen, P_{O_2} , (ii) find the order of the reaction, n , with respect to P_{O_2} , and (iii) investigate the dependence of (i) and (ii), if any, on reaction temperature as well as on the type of Saran sample under consideration. In other words, it was essential to see whether the iron-contaminated or the

TABLE 28

EFFECT OF OXIDANT FLOW RATE ON VALUES OF Q

Sample	Reaction Temperature (°C)	Oxidant	Time (min)	Q (cal/g C)				
				Flow Rate (cc/min)				
				9	14	20	30	45
S ₄ Fe	281	Air	10	12.31	12.15	11.43	12.66	12.20
S ₄ Fe	281	Air	20	16.92	17.05	16.87	17.63	17.01
S ₄ Fe	281	Air	28	18.98	19.85	18.78	20.46	19.82
S _{act}	100	O ₂	10	2.16	2.37	2.24	2.19	2.28
S _{act}	100	O ₂	20	3.05	3.26	3.15	3.29	3.10
S _{act}	100	O ₂	28	3.62	3.89	3.84	3.77	3.84

activated samples would have the same kinetic parameters (mentioned above) as the original S_4 sample.

For all runs mentioned in this section, the samples underwent the conventional heat treatment procedure and then were cooled to room temperature in N_2 flowing at 45 cc/min. Following this, each sample was held isothermally at 100°C (S_{act} and S_4Fe) or 227°C (S_4) for 30 min. During this period, a flowing mixture of O_2 and N_2 , having a known composition, was mixed in a one-liter flask. This insured the proper mixing for the two gases before they were admitted inside the DSC cell. The final flow rate of the mixture was kept constant at 45 cc/min. The partial pressures of oxygen, calculated by using the ideal gas law, were varied between 0.1 and 1.0. For each sample, an additional run was made by using air in place of the O_2 - N_2 mixture. The value of P_{O_2} for air was assumed to be 0.21.

At the end of the hold period in N_2 , the desired O_2 - N_2 mixture (or air) was admitted over the sample to replace N_2 . Q - t plots were then constructed. For each sample, the differential rate at a given reaction time t , $(\Delta Q/\Delta t)_t$, was calculated by dividing the increment of heat released ($Q_2 - Q_1$) by the corresponding time interval ($t_2 - t_1$), where t is located midway between t_1 and t_2 . Furthermore, the integral rates of heat released, $(\Sigma Q/t)_t$, were computed by directly dividing the cumulative value of heat released by the corresponding time required to reach that particular instant. The plots of these rates on a logarithmic scale versus $\log P_{O_2}$ are shown in Figures 26 and 27. For the three samples at 100 or 227°C, parallel straight lines were obtained. The same observation was true at different reaction time intervals. For all lines, the slopes were almost constant and amounted to 0.47-0.51.

Figure 26. Dependence of Differential Rates of Heat Release on $\log P_{O_2}$

Figure 27. Dependence of Integral Rates of Heat Release on $\log P_{O_2}$

This indicates that the rate of heat released is directly proportional to the square root of oxygen partial pressure. The relation is independent of reaction temperature or time. In addition, when the original carbon was activated to the 63.8% level of burn-off or contaminated with iron as an impurity, the same log-rate vs $\log P_{O_2}$ relation is valid. Thus, at 100°C where chemisorption is the only predominant process or at 227°C where simultaneous chemisorption and gasification are taking place, the reaction appears to have the same rate determining step, which is controlled by dissociation of molecular O_2 to atomic oxygen.

5.5 CARBON-OXYGEN INTERACTION AT HIGH TEMPERATURES

The TGA technique was used to study the gasification reaction of the S_4 sample with oxygen in the temperature range 450-850°C.

In brief, the sample was outgassed, flushed with N_2 at 45 cc/min, heated at 20°C/min up to 600°C, and finally kept at this temperature for 30 min. After cooling the sample to room temperature, it was held isothermally (in N_2) at the desired reaction temperature (450-800°C) for 30 min. Oxygen was then introduced to replace N_2 at the same flow rate. The decreasing weight of the sample was monitored as a function of time. For all runs, a complete burn-off (B.O.) was reached, that is, all the carbon was completely gasified (100% B.O.). A carbon having zero % B.O. is arbitrarily referred to here as the total material present prior to reaction with O_2 . Thus, moisture and volatile matter, if any, were excluded.

Previous TGA experience in this laboratory had shown that among many carbons studied in different media, the B.O. vs time plot may be affected by the height of carbon bed reacting. Therefore, this factor

was the first point to be considered. The effect of the original Saran weight on the B.O. vs time plot was studied at 575°C. The starting weights were varied between 12.8 and 21.7 mg carbon. Values of % B.O. at similar time intervals were essentially the same. For example, at 6 min reaction time, the B.O. varied between 37.5 and 37.8%, respectively. At 20 min, B.O. was 92 and 89%, respectively. This close agreement suggested that diffusional effects of O_2 down through the carbon bed were negligible. Accordingly, for all subsequent runs, a constant starting weight of about 18-19 mg was used.

5.5.1 Effect of Temperature

Typical B.O. vs t plots are shown in Figure 28 for the reaction between the S_4 sample and oxygen at 475, 500, 521, and 550°C. Each of these plots is characterized by three regions. In the first region, the rate of B.O. increases slowly with reaction time. This is attributed to activation of the carbon surface, that is, increase in specific surface area. At the end of this region, around 8-12% B.O., the second region starts where a linear relation between B.O. and time is observed up to about 55-65% burn-off. The slopes of the lines, that is, rates of gasification (or B.O.) increase with reaction temperature. The third region is associated with a decrease in gasification rate with reaction time. This region continues until the carbon is completely gasified.

At higher gasification temperatures, the general trend observed is the same. The linearity between B.O. and time, however, extends to higher values. Thus, at 575, 600, 625, 650, and 700°C, the linear regions extend to 62, 65, 71, 84, and 95% B.O., respectively. Furthermore, in the temperature region 575-650°C, as the temperature increases,

Figure 28. Gasification of S_4 Sample in Oxygen at 475-550 °C

the rate of B.O. increases. At reaction temperatures above 650°C, the rate of gasification is independent of temperature. The results are shown in Figure 29.

5.5.2 Energy of Activation-- E_a

The linearities observed in the second region of Figures 28 and 29 were further examined in the following manner. For each temperature, the rate of gasification (slope, % B.O./min) was computed. A plot of these rates on a logarithmic scale vs the corresponding reciprocals of absolute temperature (Arrhenius plots) is shown in Figure 30. Three discontinuous linear regions are observed corresponding to zones I, II, and III. Activation energies for zones I, II, and III are 42.6, 20.8, and about 2 kcal/mole, respectively. It will be indicated shortly that for zone I, the reaction rate is controlled by chemical reaction of the solid (chemisorption of O_2) and rearrangement of chemisorbed species at the surface to desorbable products. The intermediate zone is characterized by joint control of the reaction by oxygen diffusion from the exterior of the carbon surface to an active site beneath the surface, and by oxygen chemisorption. For zone III, gasification is controlled by oxygen diffusion across a relatively stagnant gas film between the exterior surface of the carbon and the main gas stream.

The linearity observed in zone I was extrapolated down to the temperature region 125-227°C. The calculated rates of gasification are given in Table 29.

A comparison between these gasification rates and those listed in Tables 21-23 show an interesting phenomenon. The rate of gasification occurring simultaneously while chemisorption is taking place (Table 21-23) is many orders of magnitude higher than that obtained from the

Figure 29. Gasification of S_4 Sample in Oxygen at 575-800 °C

Figure 30. Arrhenius Plot for Gasification of S₄ Sample in Oxygen

TABLE 29
CALCULATED RATES OF GASIFICATION FOR THE S₄ SAMPLE

Reaction Temperature (°C)	125	150	177	202	227
Gasification Rate (mg/g C/min)	4.17×10^{-11}	1.03×10^{-9}	2.18×10^{-8}	2.71×10^{-7}	2.59×10^{-6}

extrapolation of high temperature rate data (Table 29). This probably shows that more active sites which take part in gasification at lower temperatures are deactivated at higher reaction temperatures.

5.5.3 Normalization of High Temperature Reaction Rate Plots

To further examine gasification data reported in this report, Figure 31 is introduced. Here, the results were normalized in the manner described below. Values of $\tau_{0.5}$ (time to reach a fractional B.O. of one-half) directly obtained from Figures 28 and 29 were considered. At each temperature and for a reaction time t , the value of τ was calculated, where

$$\tau = t/\tau_{0.5} \quad 5.21$$

This computation was repeated at several other time intervals. The % B.O. vs the normalized reaction time τ (Figure 31) fit on one plot which is independent of reaction temperature up to B.O. < 60%. This has been confirmed in the temperature range 450-850°C. However, for B.O. > 60% and depending on reaction temperature, the linearity may be valid or it starts deviating towards lower gasification rates. The higher the gasification temperature, the longer is the linear region.

Figure 31. Normalization of Gasification Rates Using Reaction Times for 50% Burn-off

6. DISCUSSION

6.1 KINETICS OF CHEMISORPTION AND GASIFICATION

When a Saran char, like many other carbonaceous materials, is exposed to oxygen, three major reactions may occur: physical adsorption, chemisorption (formation of a stable complex at the carbon surface), and gasification to CO_2 and/or CO .

Generally speaking, at sufficiently low temperatures, physical adsorption is the predominant process. At moderate temperatures, chemisorption of oxygen is more likely to take place. As reaction temperature increases, the rate of oxygen chemisorption increases but the equilibrium amount of oxygen chemisorbed goes through a maximum as gasification becomes increasingly more important. A sharp temperature limit separating the three processes does not exist. The temperature at which a particular process is predominant depends upon the structure and purity of the carbon. For example, if the carbon has a substantial micropore system, measurable physical adsorption occurs to a high temperature. If the carbon contains large concentrations of catalytic inorganic impurities (Fe , CO ,....), gasification commences at a lower temperature.

Surface oxides formed during the oxidation of carbons have been considered by a number of investigators. For example, Bonnetain and Hoynant (110), from their study on graphite, showed that combustion products during a gasification run (CO/CO_2 ratio) were similar to those obtained during desorption of chemisorbed oxygen at comparable temperatures. They concluded that gasification proceeds by continuous formation and desorption of surface oxides. Laine et al. (33, 34) studied gasification and continuous formation of surface oxides on

Graphon. They concluded that formation of surface oxides, far from being an intermediate step, retards the gasification step by occupying part of the active surface area. Both groups found that gasification of a carbon previously deoxygenated at 950°C began at a high rate which subsequently declined. Bonnetain attributed the initial high rate to the "clean up" of labile carbon atoms and stressed the subsequent period of slower steady state gasification. Laine et al., referring to the period of declining rate, proposed an equation relating the rate of carbon burn-off (dC/dt which is equivalent to dW_-/dt in the present work) to the active surface area (ASA) and fractional surface coverage (θ). This is given by

$$-(dW_-/dt) = k_- P_{O_2} (ASA) (1 - \theta) \quad 6.1$$

where k_- and P_{O_2} are the rate constant for gasification (Laine et al. used the symbol k instead of k_-) and oxygen pressure, respectively.

Vastola et al. (35) showed that the equation was only approximate and that the oxide may participate to a small degree in gasification. The so-called stable surface oxides are only "relatively" stable, and there is continuous decomposition and reformation of these oxides contributing to gasification. This was accounted for in a revised form of equation 6.1:

$$-dW_-/dt = k_- P_{O_2} (ASA) (1 - \theta) - \Pi (\theta) (dW_-/dt) \quad 6.2$$

where Π is temperature dependent, increasing from 0.2 to 0.4 as reaction temperature decreases from 625°C to 550°C. It is noteworthy that as reaction temperature decreases, a steady increase in the value of Π would make the value approach unity at temperatures close to 100-225°C. Accordingly, equation 6.2 would be reduced to

$$-dW_-/dt = k_- P_{O_2} (ASA) \quad 6.3$$

As will be indicated shortly, applicability of equation 6.2 to the present study is not valid in the case of Saran chars. However, it is probably that these chars gasify at low temperatures via the continuous decomposition and reformation of surface oxides.

Lussow et al. (61, 62) suggested that oxygen molecules react with carbon surfaces to form a mobile transition state complex $[C_2(O_2)^*]$ which dissociates giving two mobile chemisorbed oxygen atoms $[C(O)^*]$. These species may form a relatively stable surface oxide or gasify directly to CO_2 and CO . The steady state concentration of the mobile complexes is small. It may be speculated that these species could be O_2^- or O^- ions formed by electron transfer from the valence band of the carbon to the oxygen species. This is supported by the observed decrease in the magnitude of spin centers (41) and electric conductivity (185) upon adsorption of oxygen.

It appears that all previous workers agree that some surface oxides are formed during the gasification of carbons, the amount of which is dependent upon temperature, pressure, and type of carbon used. In the present study, chemisorption of oxygen was the main concern. Yet, the results indicate that gasification products are being evolved during chemisorption above $100^\circ C$. This situation makes it uncertain whether the results should be interpreted in terms of either "chemisorption" or "gasification." Added to this complexity are the data obtained here for gasification of Saran char at $450-850^\circ C$, cf. Section 5.5. For example, a value of $E_a = 42.6$ kcal/mole (cf. Figure 30) for the S_4 sample is typical for carbon gasification by oxygen. In this connection, higher values of E_a determined for CO evolution from surface oxides (70-112 kcal/mole) (155) are excluded.

6.1.1 Activation Energy for Gasification, E_a^- -S₄ Sample

For the S₄ sample, the calculated weights of carbon gasified during chemisorption, W_- (mg gasified/g C), were plotted versus reaction time at several temperatures. For each W_- , the corresponding value of θ was determined by knowing total weight of oxygen uptake, W_+ (mg oxygen/g C), and by using equation 4.7. The calculated rates (dW_-/dt) and (W_-/t) at constant coverage were computed for $0.97 > \theta > 0.82$. Arrhenius plots for cumulative rates are shown in Figure 32. For values of $\theta = 0.82, 0.88, 0.93$, and 0.97 , the corresponding values of E_a^- are 17.2, 14.8, 14.4, and 14.4 kcal/mole. For differential rates (dotted line), E_a^- is 14.4 kcal/mole at $\theta = 0.88$. It is seen that: (i) the value of E_a^- is almost independent of coverage (ignoring the lowest coverage where the rates were substantially lower and thus have some uncertainty), and (ii) the average value of E_a^- (15.3 ± 1.5 kcal/mole) is relatively small compared to the 42.6 kcal/mole (cf. Figure 30) determined at 450-550°C. This explains the fact that rates of early gasification (at 125-227°C) are many orders of magnitude higher than those obtained by extrapolation of higher temperature gasification data to this temperature range (cf. Tables 21-23, 29).

Values of W_+ and W_- are calculated by using method II (Section 5.3.4.2) where it was assumed that CO₂ had been the only gas evolved. The experimental weight, W_{exp} , directly recorded from the TGA unit is given by

$$W_{exp} = W_+ - W_- \quad 6.4$$

6.1.2 Activation Energy for Chemisorption, E_a^+ -S₄ Sample

For oxygen chemisorption, plots of W_+ versus reaction time showed that oxygen uptake is rapid at the beginning of a run but the rate slows

Figure 32. Arrhenius Plots for Gasification at Constant Coverage--S₄ Sample

down with time. This is true for either differential rates (dW_+/dt) or cumulative rates (W_+/t). Arrhenius plots were also made at constant values of θ (cf. Figure 33). Values of E_a^+ at $\theta = 0.76, 0.82, 0.88, 0.93$, and 0.97 are 11.8, 10.6, 10.9, 11.1, 11.6, and 11.4 kcal/mole, respectively. Therefore, when the cumulative rates of chemisorption are considered, an average value of $E_a^+ = 11.2 \pm 0.6$ kcal/mole is obtained, which is independent of θ or reaction temperature. A similar trend was observed for the differential rates. This is shown in Figure 34 where values of E_a^+ are scattered around an average value of 11.4 ± 0.7 kcal/mole. Therefore, for the S_4 sample, one may propose

$$(W_+/t)_\theta = B_+ \exp (-E_a^+/RT) \quad 6.5$$

$$(dW_+/dt)_\theta = b_+ \exp (-E_a^+/RT) \quad 6.6$$

where B_+ and b_+ are constants for each coverage, but E_a^+ is independent of θ . Combining 6.5 and 6.6, and upon integration, one gets

$$W_+ = (t)^{(b_+/B_+)} \quad 6.7$$

6.1.3 Activation Energy for Chemisorption, $E_a^+ - S_{act}$ Sample

Dependence of $\log (dW_+/dt)_\theta$ or $\log (W_+/t)_\theta$ on $(1/T)$ is shown in Figure 35 for the S_{act} sample. Two observations are noted: (i) whether cumulative or differential rates are considered at a given coverage, the activation energy is the same, and (ii) as θ increases, E_a^+ increases and finally attains an almost constant value (for $\theta = 0.71, 0.75, 0.80$, and 0.85 , E_a^+ are 7.2, 10.8, 14.7, and 15.0 kcal/mole, respectively). The increase in E_a^+ with coverage is attributed to the probability of collisions between gas molecules and active sites in the char accessible to the gas (oxygen). In this regard, one may refer to

Figure 33. Arrhenius Plots for Oxygen Chemisorption on S_4 Sample--Cumulative Rates

Figure 34. Arrhenius Plots for Oxygen Chemisorption on S_4 Sample--Differential Rates

Figure 35. Arrhenius Plots for Oxygen Chemisorption on S_{act} Sample

the Langmuir equation which assumes that: (i) adsorption takes place through collision of gas molecules with vacant sites, (ii) energy of adsorbed species is independent of θ (requiring the adsorbent surface to be uniform), and (iii) heat of adsorption is independent of θ .

Apart from the physical significance of θ which could be misleading (as will be indicated later), conditions (ii) and (iii) are true for the S_{act} sample above 125°C and the S_4 sample above 100°C. These are the limits at which gasification commences on each sample. It is suggested, therefore, that during gasification, new vacant sites are continuously being generated. Chemisorption of oxygen on those sites would require a lower activation energy than on the "old" sites. The competition maintains the observed value of E_a^+ constant.

For condition (i), that is, collision of gas molecules with vacant sites, the author refers to Figure 1. While moving from gas phase (point a) to adsorbed layer (point f), the molecules pass over a potential energy barrier, the height of which is equal to E_a^+ . There are also some molecules in the activated state at the top of the barrier which are in equilibrium with those at a. These activated-state molecules are known to vibrate to and away from the surface; either forming carbon-oxygen complex or returning to original gaseous state (oxygen molecules). The rate of adsorption is given by multiplying frequency of vibration by the concentration of activated molecules. On this basis, the full kinetic derivation was made (186), which can be presented here as

$$dW_+/dt = \frac{\sigma}{\sqrt{2\pi mkT}} \cdot f_-(\theta) \cdot P \cdot \exp(-E_a^+/RT) \quad 6.8$$

which indicates that rate of adsorption is directly proportional to (i) pressure of the gas (determines number of collisions with the

surface), (ii) a fractional coverage term $f(\theta)$, and (iii) a steric factor σ (fraction of total number of colliding molecules possessing the appropriate orientation with active sites). From kinetic theory of gases, the term $P/\sqrt{2\pi m kT}$ defines the number of molecules of mass m striking unit area of surface per unit time at temperature T .

Depending on the adsorbent-adsorbate system, the term $f(\theta)$ could have three different forms: (i) when the adsorbed molecule occupies a single site on adsorption, $f(\theta) = (1 - \theta)$, (ii) if the molecule dissociates on adsorption to two atoms, each occupying a single site with a mobile layer of adsorbate atoms (say 0 atoms), then $f(\theta) = (1 - \theta)^2$, and (iii) for dissociative adsorption [similar to (ii)] but the layer is immobile, the term $f(\theta)$ becomes

$$f(\theta) = z(1 - \theta)^2 / (z - \theta) \quad 6.9$$

where z is the number of nearest neighbor sites.

The numerical values of E_a^+ (10-15 kcal/mole) indicated in Figures 33-35 are in excellent agreement with those reported in the literature. Bansal et al. (39) from their study on oxygen chemisorption on an ultraclean Graphon surface, outgassed at 1000°C and a pressure better than 10^{-8} Torr, concluded that five groups of active sites existed. The activation energy, being constant for each group of sites, increased abruptly in going from one group to another (from 3.1 to 12.4 kcal/mole). For the least active group of sites ($E_a^+ = 12.4$ kcal/mole), values of θ were greater than 0.47. With the present data on Saran chars pretreated in N_2 at 600°C and at a pressure of about 0.01 Torr, it is suggested that oxygen is chemisorbed on the least active group of sites during the DSC or TGA runs.

Allardice (57), from his studies of oxygen adsorption on brown coal chars at 25-200°C, found that chemisorption conformed to the Elovich equation (Section 2.1.5). He reported an apparent activation energy of 11.1 ± 1.5 kcal/mole, which was independent of θ . This is in good agreement with the present results on the S_4 sample, yet no gasification products were detected below 250°C (57). He suggested migration of physically adsorbed species over the char surface to the active sites where chemisorption took place. This mechanism is not true with Saran chars, since no physical adsorption was observed in this study above 100°C.

6.1.4 Effect of Pressure-- S_4 and S_{act} Samples

It is now of interest to investigate the relations between dW_+/dt and P_{O_2} found in this study. It is remembered that in Section 5.4.4 (Figures 26 and 27) linearities between $(dQ/dt)_{t,T}$ or $(Q/t)_{t,T}$ versus P_{O_2} on a log-log scale were found, the plots having the forms

$$(dQ/dt)_{t,T} \sim \sqrt{P_{O_2}} \quad 6.10$$

and

$$(Q/t)_{t,T} \sim \sqrt{P_{O_2}} \quad 6.11$$

Even though these plots are of empirical interest, they lack fundamental importance since along each plot, θ was varying. To obtain the fundamental relationship between rate and pressure, either the variation in θ should be taken into consideration or θ should be held constant.

Figure 36 presents plots of Q versus t for the S_{act} sample determined at 100°C and at different oxygen pressures. Similar plots were obtained for the S_4 sample at 100°C. At fixed values of Q and, hence, θ , times to reach Q at different pressures can be determined. Also, at

Figure 36. Dependence of Q (cal/g C) at 100°C on Oxygen Pressure-- S_{act} Sample

fixed values of Q , slopes of the plots $(dQ/dt)_Q$ at different pressures can also be determined. Selected values are presented in Figure 37. The plots are closely parallel, with slopes varying between 0.95 and 1.03. That is, at constant θ

$$(dQ/dt)_{\theta,T} \sim P \quad 6.12$$

Since at 100°C, the rate of gasification is negligible

$$(dQ/dt)_{\theta,100} \sim (dW_+/dt)_{\theta,100} \quad 6.13$$

$$\text{Hence, } (dW_+/dt)_{\theta,100} \sim P \quad 6.14$$

in conformity with equation 6.8.

6.1.5 Surface Coverage Term, $f(\theta)$, S_4 and S_{act} Samples

Relationships between either chemisorption rates, gasification rates, or overall rates of weight increase versus $f(\theta)$ can now be considered. For the S_4 sample, plots of these rates versus $(1 - \theta)$ at different temperatures between 100 and 227°C were not linear. However, the cumulative rates, when plotted against $(1 - \theta)^2$, were linear as seen in Figures 38-40. Likewise, for the S_4 sample, differential rates versus $(1 - \theta)^2$ were also linear as shown in Figures 41-43. Based on theory, it is concluded from this relationship that oxygen chemisorption is dissociative with one oxygen atom occupying a carbon site. Further, the atoms of oxygen are mobile on the carbon surface and tend to spread out evenly on the active sites as a result of the repulsion forces which exist between them.

For the S_{act} sample, gasification data were not very reliable due to the low rates. Thus, only values of W_+ were of concern for this sample. In contrast to the findings for the S_4 sample, plots of cumulative or differential chemisorption rates versus $(1 - \theta)^2$ were not

Figure 37. Effect of Oxygen Partial Pressure on $(dQ/dt)_Q$ and $(1/t)_Q$

Figure 38. Dependence of Cumulative Rates of Oxygen Chemisorption on Surface Coverage-- S_4 Sample

Figure 39. Dependence of Cumulative Rates of Early-Gasification on Surface Coverage--S₄ Sample

Figure 40. Dependence of Cumulative Experimental Rates on Surface Coverage--S₄ Sample

Figure 41. Dependence of Differential Rates of Oxygen Chemisorption on Surface Coverage--S₄ Sample

Figure 42. Dependence of Differential Rates of Gasification on Surface Coverage--S₄ Sample

Figure 43. Dependence of Differential Experimental Rates on Surface Coverage--S₄ Sample

linear. However, as seen in Figures 44 and 45, plots of (W_+/t) and (dW_+/dt) versus $[z(1 - \theta)^2/(z - \theta)]$ were linear, where z , the number of nearest neighbor sites, is taken as equal to two. In the case of trigonally bonded carbon solids, this is the expected value because of the large distance (and weak interaction) between basal planes. This relationship suggests that oxygen chemisorption is again dissociative with one oxygen atom per carbon site, but that the chemisorbed oxygen is immobile on the surface of the activated Saran sample. Activation of carbons has been shown to decrease the mobility of physically adsorbed xenon and chloroplatinic acid on carbon surfaces (187, 188).

According to the data shown in Figures 37-45, the following equation is suggested for differential rates of oxygen chemisorption on Saran chars

$$(dW_+/dt) = [k_+] [f(\theta)] [ASA] [C_{O_2}] + I \quad 6.15$$

where k_+ is the differential rate constant for oxygen chemisorption (cm/sec), ASA is active surface area (cf. Table 3), C_{O_2} is the concentration of oxygen (moles/cc), and I is the intercept (moles/sec).

Similar equations can be obtained for (i) differential gasification rates (dW_-/dt) with k_- replacing k_+ in 6.15, (ii) cumulative chemisorption rates (W_+/t) , and (iii) cumulative gasification rates (W_-/t) .

For cases (ii) and (iii), the rate constants are k'_+ and k'_- , respectively. Furthermore, according to 6.4, two more rate equations can be assigned to ascribe the actual experimental rates (dW_{exp}/dt) and (W_{exp}/t) .

For the S_4 sample, values of k_+ , k_- , k'_+ , and k'_- are shown in Table 30, while those for the S_{act} sample (k_+ and k'_+) are given in Table 31. For oxygen chemisorption, ratios of k_+ and k'_+ values for S_{act} and S_4

Figure 44. Dependence of Cumulative Rates of Oxygen Chemisorption on Surface Coverage-- S_{ac} Sample

Figure 45. Dependence of Differential Rates of Oxygen Chemisorption on Surface Coverage-- S_{ac1} Sample

TABLE 30

DIFFERENTIAL AND CUMULATIVE RATE CONSTANTS* FOR THE S₄ SAMPLE

Temp. (°C)	100	125	150	177	202	227
k ₊	0.070	0.651	1.092	1.628	3.774	7.892
k' ₊	0.142	0.788	1.702	3.145	6.938	10.249
k ₋	0	~0	0.099	0.211	0.611	1.051
k' ₋	0	~0	0.115	0.281	0.918	1.750
* x 10 ⁻⁸ cm/sec						

TABLE 31

DIFFERENTIAL AND CUMULATIVE RATE CONSTANTS* FOR
OXYGEN CHEMISORPTION ON THE S_{act} SAMPLE

Temp. (°C)	75	100	125	150	177
k ₊	4.05	4.96	6.75	9.72	13.31
k' ₊	5.78	6.82	8.28	14.10	29.20
* x 10 ⁻⁸ cm/sec					

samples are shown in Table 32. The rate constant for oxygen chemisorption k₊ on the S_{act} sample is higher than that for the S₄ sample at all temperatures. In contrast, the gasification rate for the S₄ sample was higher than that for the S_{act} sample at all temperatures studied. This suggests that gasification, leading to the production of carbon dioxide, is accelerated when the oxygen complex is mobile on the carbon surface.

Consideration is now given to values of I in equation 6.15. For differential rates on the S₄ sample, values of I for chemisorption are -0.010, +0.017, +0.031, and +0.0101 mg/g C/min, and for gasification

TABLE 32

RATIOS OF k_+ AND k'_+ FOR THE S_{act} AND THE S_4 SAMPLES

Temp. ($^{\circ}\text{C}$)	100	125	150	177
k_+/k_+	70.9	10.4	8.9	8.2
k'_+/k'_+	48.0	10.5	8.3	9.3

are 0.003, 0.008, 0.019, and 0.043 mg/g C/min at 150, 177, 202, and 227 $^{\circ}\text{C}$, respectively. For oxygen chemisorption on the S_{act} sample, these values are -0.152, -0.132, -0.114, -0.034, and +0.068 mg/g C/min at 75, 100, 125, 150, and 177 $^{\circ}\text{C}$, respectively.

It is thought that the presence of an intercept in the rate equation is due to the difficulty in calculating absolute values of θ (or W_{ASA}) as described in Section 4.1.3.2. The total active surface area (ASA) was determined by first outgassing the char at 950 $^{\circ}\text{C}$ under ultrahigh vacuum conditions, chemisorbing oxygen on the active sites at 100 $^{\circ}\text{C}$, and then recovering the complex as CO and CO₂ by subsequent heating to 950 $^{\circ}\text{C}$. That is, oxygen uptake was carried out in the absence of carbon gasification (at 100 $^{\circ}\text{C}$). However, rates of chemisorption which have been calculated for temperatures above 100 $^{\circ}\text{C}$ are those for which gasification of carbon was occurring simultaneously with chemisorption. The total effective active surface area in the presence of gasification is expected to be different from that in absence of gasification, as previously discussed by Hart *et al.* (37). Thus, there will be uncertainty as to the absolute values of θ where chemisorption and gasification are occurring simultaneously. Indeed, as will be seen shortly, θ values greater than 1.0 were found for interaction with oxygen on the S_4 sample at the higher temperatures used in this study.

Also, it is recalled that it was necessary to have values for the total oxygen chemisorbed at infinite time (W_{tot}) at each reaction condition in order to calculate θ as a function of time during the experimental runs. It was only possible to obtain such data at 100°C (in the absence of gasification) when using the TGA apparatus. In 48 hr, equilibration was closely reached. Values of total oxygen chemisorbed at infinite time at temperatures above 100°C were assumed to be equal to the value obtained at 100°C. In fact, such is expected not to be strictly the case, that is, concurrent gasification is expected to alter the total amount of oxygen chemisorbed.

By trial and error, it appears that values of W_{ASA} and W_{tot} can be found such that each plot giving the relation between the differential rate and $f(\theta)$ goes through the origin and remains a straight line. For example, for the plot at 202°C in Figure 41, if W_{ASA} and W_{tot} are assumed to be 12% higher than the values taken from previous measurements at 100°C (as first described), the line passes through the origin and is parallel to the original straight line.

A different approach is now considered to correlate values of W_+ and W_- to θ . For each reaction temperature, two observations were noted: (i) the ratio W_+/W_- decreases with time, thus indicating that the relative increase in carbon gasified is exceeding that of oxygen chemisorbed on the S_4 sample (still both W_+ and W_- were increasing) and (ii) W_+/W_- at particular time intervals decreases with an increase in temperature. Attempts were made to correlate this ratio (or dW_+/dW_-) with other experimental parameters (temperature, time, θ). The most meaningful information found is shown in Figure 46 for the S_4 sample. Since the atomic weights of oxygen and carbon are 16 and 12,

Figure 46. Variation of (dW_+/dW_-) with Surface Coverage--S₄ Sample

respectively, the term $(0.75 \, dW_+/dW_-) = (O/C)$ gives the ratio between the number of oxygen atoms chemisorbed to that of carbon atoms gasified. Values of O/C decrease rapidly with increasing coverage up to about $\theta = 0.8$. As the "apparent" values of θ approach unity, the ratio O/C levels off to 2.0. The data points shown in the figure correspond to five reaction temperatures. Therefore, independent of temperature, the ratio O/C becomes equal to 2.0, near the conventionally so called "saturation conditions." When this is reached, chemisorption of two oxygen atoms occurs concurrently with gasification of one carbon atom. Since at such low temperatures, CO_2 is far in excess of CO in the product gas, it means that essentially half of the oxygen is forming chemisorbed complex at the surface while the other half is going to gaseous products. It is noted that for reaction at $227^\circ C$, θ is calculated to exceed 1.0. This means that more complex is forming concurrent with gasification than is forming on an ultraclean surface in the absence of gasification. Such a phenomenon has been reported by Hart *et al.* (37).

Further considerations were given to test the applicability of Elovich equation(s) (Section 2.1.5) to the present data on Saran chars. Unlike the S_4 sample, the S_{act} sample showed a linearity between W_+ and $\log t$ for each reaction temperature as seen in Figure 47. At 75, 100, 125, 150, and $177^\circ C$, slopes amounted to 0.69, 1.14, 1.60, 2.29, and 3.36 mg/g C, respectively. The corresponding values of α (cf. equation 2.10) amounted to 3.34, 2.02, 1.44, 1.01, and 0.69, respectively. For each line, the intercept, $\frac{2.303}{\alpha} \log (\alpha\alpha)$, was determined. Initial rates of oxygen chemisorption, that is, values of a (cf. equation 2.9) are 0.281, 0.418, 0.634, 1.172, and 1.889 mg/g/min at 75, 100, 125, 150, and

Figure 47. Elovich Plots for Oxygen Chemisorption on S_{act} Sample

177°C, respectively. The continuity in each line suggests that when oxygen is chemisorbed on the S_{act} sample, only one group of active sites is existing at the char surface.

6.2 VALUES OF ΔH

The physical significance of ΔH values, obtained for different carbons exposed to oxygen, is a complex function which depends on several factors. The situation is rather simple in the case of a gas-metal system where one or two values of ΔH are obtained. Such values are in good agreement with the calculated ones determined via considering different types of bonds broken or formed during adsorption. In the case of carbons, however, particularly when exposed to oxygen, several types of single and complex groups are formed, among these are carbonyl and lactone groups. Even for lactones, the C-O-C link may be attached to a four- or five-membered ring with the carbonyl group arbitrarily assigned to more than one possible position. Added to this complexity is the structure of the adsorbent surface, which may vary between the simple ordered well defined crystal type system (diamond or graphite) and the complex disordered structure of microporous carbons and chars.

Saran char carbonized in an inert atmosphere at 1000°C contains 65% highly perfect and graphite-like layers, the remainder being less organized (189). About 55% of the graphite-like layers are in pairs with an interlayer spacing of 3.7 Å, the remainder having no related orientation (189). A crystallite size of about 20 Å in diameter is reasonable to represent the basal plane surface of a Saran char. This is shown in Figure 48, with horizontal edges indicating zig-zag configuration and vertical edges indicating arm-chair configuration.

Figure 48. Electronic Configuration and Structural Parameters of a Saran Crystallite ($\sim 20\text{\AA}$ in Diameter)

Also, indicated are some fragment carbon atoms protruding from the surface, each of which is attached to another carbon atom. Imperfections in the basal planes such as vacancies, dislocations, and impurities, are excluded from consideration for simplicity. The C-C distance of 1.42 Å suggests the existence of conjugated single and double bonds within the hexagons. This means that each carbon atom is attached to another carbon by a σ bond. The delocalized electrons, called π electrons and responsible for forming π bonds, are partially unpaired, thus giving rise to spin centers. The gain in stability due to delocalization of the π electrons, generally known as resonance energy, may vary between 9 and 12 kcal/C atom (190, 191). These values were either calculated or determined experimentally. A value of 10.5 kcal/C atom will be used here for the calculations that follow.

The formation of some functional groups is shown in Figure 49 at different locations. For many organic compounds, the bond energy (B.E.) for the (C=O) group varies between 165 and 175 kcal/mole. An average value of 170 kcal/mole is used here. Values of B.E. for (C-O), (C-C), (C=C), and (O=O) are assigned as 82, 83, 148, and 118 kcal/mole, respectively (192). Using these values along with 10.5 kcal/C atom (for resonance energy), values of ΔH (kcal) for chemisorption of one mole of oxygen are calculated. Details concerning these calculations are given in the Appendix. For structures A and B (carbonyl), C and D (lactones), and E (as suggested by Puri, cf. 111 and 193), values of ΔH are 71, 146.5, 216, 216, and -9.5 kcal/mole oxygen, respectively.

It is seen, therefore, that for oxygen chemisorption on carbons, simple calculations fail to give a unique value for ΔH . Even for any

Figure 49. Formation of Different Carbon-Oxygen Complexes on Edges of Basal Plane of Saran Crystallite

of the five structures mentioned above, there are some other factors and parameters to be considered, which will affect ΔH . These are:

1. The electronic structure for boundary atoms are not the same (190). Three different types of atoms exist: (i) atoms like (z) (cf. Figure 48) which may revert to a divalent state thus losing their unpaired electron character, (ii) atoms as (a) which could acquire a partial triple bond character by partial pairing of the unpaired electrons, and (iii) fragment atoms, (f), having an unpaired valence orbital occupied by one electron (as in the case of free radicals).

2. The paramagnetism of the surface is continuously decreasing due to the adsorption of oxygen (paramagnetic) atoms, thus, the concentration of spin centers at the edges of the crystallite is decreasing. This has been confirmed by ESR studies (194, 195) and by the ortho-para hydrogen conversion techniques combined with H_2/D_2 equilibration (11).

3. The heterogeneity of the carbon surface is partly due to the existence of different groups of active sites (39, 65, 125) and also because of lattice imperfections (dislocations, vacancies, etc.).

4. The presence of impurities (mostly Fe, Co, Ni, Ca, Mg) exist either at basal planes or between them. The role of such metals is generally to catalyze the carbon-oxygen reaction; however, it is not yet understood whether they enhance or decrease the relative rates of formation of one structure (A to E) compared to others.

5. Crystallite size, free valencies, and bond orders can vary. This is clarified by referring to the electronic properties of some condensed aromatic compounds consisting only of fused benzene rings (191). Once more, Figure 48 is considered. Rings (1-2), (1-3), (1-4),

(1-6), (1-7), and (1-8) represent naphthalene, anthracene, naphthacene, pentacene, hexacene, heptacene, and octacene, respectively. Further complex molecules were also considered (191) such as corene (rings 2, 3, 9, 10, 11, 17, and 18), ovalene (2-4, 9-12, and 17-19), circumanthracene (2-5, 9-13, and 17-20), and even larger molecules up to 25 fused rings. These compounds could be viewed, more or less, as carbons having different crystallite sizes. Following the linear combination of atomic orbital calculations (molecular orbital theory) made for these compounds, values of free valencies (represented by dotted arrows in Figure 48) and bond orders (simply considered as bond lengths) were computed for each atom in every separate compound. For example, the free valence pointing out of ring number 3 would have different reactivities towards the same reagent (substitution or addition reactions) depending upon the size of molecule to which the ring is attached. In general, the larger the molecule (or crystallite size of carbon), the higher is the maximum free valence, the smaller is the bond order, and therefore, the more reactive would this molecule (or carbon) be. Furthermore, with increasing the size of aromatic hydrocarbons, the mean bond order decreases (which corresponds to steady lengthening of C-C distance from benzene to octacene, for example), but the mean valence decreases. This means that as the size of the platelet increases, the spread between the maximum and minimum values of free valencies in particular edge carbon sites increases (191).

It is concluded at the present time that numerical values of ΔH obtained experimentally cannot be easily used to characterize the carbon surface or to interpret data in terms of bond-energies.

7. SUMMARY, CONCLUSIONS AND SUGGESTIONS FOR FUTURE STUDY

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to study exothermicity and kinetics of interaction between Saran chars and oxygen at selected isothermal temperatures in the range 75-850°C. Three Saran chars, particle size (150 x 250) mesh, were used: (i) original unactivated char (S_4), (ii) same char but associated with iron as an accidental contaminant introduced through grinding in stainless steel gears ($S_4\text{Fe}$ sample), and (iii) an air activated char (S_{act}) prepared by gasifying the S_4 sample in air to a 63.8% level of burn-off.

Most chars were characterized by determining: (a) active surface areas (ASA), (b) BET surface areas, (c) CO_2 surface areas, and (d) mercury densities. Values of a, b, and c are: (i) 37, ~ 825 , and 1150 for the S_4 sample, and (ii) 52, ~ 1250 , and 1240 m^2/g for the S_{act} sample. Mercury densities are 1.27, 1.15, and 0.94 g/cc for S_4 , $S_4\text{Fe}$, and S_{act} chars, respectively.

When a char is exposed to oxygen at an isothermal temperature, the DSC output determines the amount of heat released, Q (cal/g C), while the TGA technique monitors the change in weight, W_{exp} (mg/g C), associated with the reaction. At 100°C, chemisorption of oxygen (molecular weight = 32) is the only process taking place. Therefore, $W_{\text{exp}} = W_+$, where W_+ is the weight of oxygen uptake (mg/g C). Values of ΔH (kcal/mole) are then calculated by: $\Delta H = 32 Q/W_{\text{exp}}$.

For the interaction between oxygen and Saran chars, many values of ΔH can be experimentally measured. These are substantially affected by: (i) desorption conditions applied to the char (for example, desorption temperature, T_{des} , and time, t_{des}) prior to exposure to oxygen,

(ii) history of sample, that is, the number of desorption-adsorption cycles, (iii) surface coverage, θ , (iv) reaction temperature, T , (v) partial pressure of oxygen, P_{O_2} , (vi) type of reaction(s) occurring at the char surface (physical adsorption, chemisorption, gasification to CO and/or CO₂), and (vii) nature of the groups formed at the surface. Under an arbitrary standard pretreatment procedure [heating in N₂ (45 cc/min) at 20°C/min up to T_{des} of 600°C, then holding at T_{des} for 30 min], values of ΔH at $P_{O_2} = 1$, measured on fresh Saran samples at $T = 100^\circ\text{C}$, were 42 ± 1 , 68 ± 2 , and 75 ± 2 kcal/mole for the S_4 , $S_4\text{Fe}$, and S_{act} chars, respectively. Below 100°C, physical adsorption of oxygen occurred simultaneously with chemisorption, while above 100°C, gasification reaction(s) also took place.

Conditions (i), (ii), (iv), and (vi) were investigated on the S_{act} char. The effect of desorption temperature (at $t_{des} = 30$ min) prior to subjecting the fresh sample to oxygen at $T = 100^\circ\text{C}$ and $P_{O_2} = 1$ atm indicated that ΔH was 60 ± 2 , 58 ± 3 , 66 ± 1 , 77 ± 2 , and 81 ± 3 kcal/mole for T_{des} of 450, 500, 550, 600, and 700°C, respectively. Variation of t_{des} during pretreatment (at $T_{des} = 600^\circ\text{C}$) of a fresh S_{act} sample, followed by exposure to oxygen ($P_{O_2} = 1$) at 100°C showed an interesting observation. Increase of t_{des} from zero to 10 hr decreased both the subsequent value of Q or W_{exp} , however, the corresponding values of ΔH remained constant at a value of 76 ± 2 kcal/mole. It is believed that longer t_{des} increases the fraction of unoccupied active sites available for oxygen chemisorption, but increased annealing decreases the total number of active sites (occupied and unoccupied).

Condition (iv) was tested on the three Saran chars. At a given T above 125°C , values of ΔH , calculated as mentioned earlier, increased with reaction time. This suggested that gasification of carbon was occurring concurrently with oxygen chemisorption. Thus, $W_{\text{exp}} = W_+ - W_-$, where W_- is weight of carbon gasified. To calculate values of W_- , four methods were proposed. The most reasonable method is based on the assumption that at $T = 125\text{--}227^{\circ}\text{C}$, CO_2 (rather than a mixture of CO and CO_2) is essentially the only gas evolved during gasification.

Kinetics of oxygen chemisorption and/or gasification were investigated in two temperature regimes: $75\text{--}227^{\circ}\text{C}$ and $450\text{--}850^{\circ}\text{C}$. For the first regime, $W_+ > W_-$, and, therefore, the weight of char during exposure to oxygen, or W_{exp} , progressively increased with reaction time. Cumulative rates, (W_+/t) and (W_-/t) , as well as differential rates, (dW_+/dt) and (dW_-/dt) , increased with increasing T ; but they decreased with reaction time. On the other hand, for the high temperature regime, $W_- \gg W_+$, that is, the weight of oxygen chemisorbed was negligible compared to that of carbon gasified. At a given T , say 500°C , the rate of gasification of the S_4 sample increased with t up to $\sim 10\%$ burn-off, then became linear to $\sim 60\%$. Thereafter, the rate declined until complete burn-off (100%) was reached. The linear gasification rates were considered. Arrhenius plot between $T = 723$ and 1123°K showed three linear regions corresponding to reaction zones I, II, and III. Activation energies for zone I ($450\text{--}550^{\circ}\text{C}$), II ($550\text{--}650^{\circ}\text{C}$), and III ($650\text{--}850^{\circ}\text{C}$) were 42.6, 20.8, and ~ 2 kcal/mole, respectively. The data conforming to zone I were extrapolated to the low temperature regime where rates of gasification were estimated. Estimated rates

were at least several orders of magnitude smaller than gasification rates found experimentally at the lower temperatures, that is, below 227°C.

For the low temperature regime, kinetics of oxygen chemisorption or carbon gasification followed a Langmuir-type rate equation. That is, the rate is proportional to a surface coverage term, concentration of oxygen, and ASA. It was concluded that oxygen was dissociatively chemisorbed at the char surface with formation of a mobile layer on the S_4 sample or an immobile layer on the S_{act} sample. Values of activation energy for chemisorption, E_a^+ , and gasification, E_a^- , were computed for the low temperature regime. For the S_4 sample, values were 11.3 ± 0.5 and 15.3 ± 1.5 kcal/mole, respectively, and were independent of θ . For the S_{act} sample, values of E_a^+ at $\theta = 0.71, 0.75, 0.80$, and 0.85 were 7.2, 10.8, 14.7, and 15.1 kcal/mole, respectively.

For the S_4 sample, the ratio of the instantaneous rate of oxygen chemisorption to carbon gasification was a function of θ and independent of T between 125 and 227°C. Up to $\theta = 0.9$, the ratio decreased sharply with increasing θ . Above $\theta = 0.9$, the ratio was essentially constant, with the chemisorption of two oxygen atoms occurring simultaneously with the gasification of one carbon atom.

Unlike the S_4 sample, oxygen chemisorption on the S_{act} char followed an Elovich type equation: $W_+ = \alpha \log t + a$, where α (slope) and a (intercept) were temperature dependent.

The DSC technique was also used to investigate the dependence of Q on other experimental parameters (oxidant flow rate, carbon bed height, and particle size). The study indicated that the dependence

of Q on mass transfer rate of oxygen through the reaction chamber, or through the char bed or inside the pores of the char was insignificant.

The effect of P_{O_2} on Q was studied for the S_{act} and S_4 samples at 100°C and for the S_4Fe sample at 281°C. At 100°C, plots of $\log (dQ/dt)$ at constant reaction time versus $\log P_{O_2}$ were linear with slopes varying between 0.47 and 0.51. However, when the plots were made between $\log (dQ/dt)$ at constant values of Q versus $\log P_{O_2}$, linearities were also observed with slopes scattered around one.

Application of DSC and TGA techniques should be extended to study interaction of oxygen with coal chars. It is of interest to correlate the heat of interaction of coal chars with oxygen at low temperatures with their reactivities towards gasification at elevated temperatures. DSC studies on coal-oxygen interaction will shed additional light on the nature of the chemical reactions occurring in this important (commercial) process. Further, it is hoped that with this new technique, the mechanism of coal-char gasification will be better understood.

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9. APPENDIX A

CALCULATIONS OF ΔH (kcal/mole oxygen) VALUES

1. Values of Bond Energies (cf. References 190-193)

<u>Bond</u>	<u>Bond Energy (kcal/mole)</u>
C=O	170
C-O	82
C-C	83
C=C	148
O=O	118
O-O	39
Resonance energy (average)	10.5

2. Formation of Structure (A) (cf. Figure 50)

1. Break O=O:	118
2. Two C=C go to two C-C: $2 \times 65 =$	130
3. Loss of resonance energy $2 \times 10.5 =$	<u>21</u>
Total	269
4. Formation of two C=O: $2 \times 170 =$	340

$$\Delta H = 269 - 340 = -71 \text{ kcal}$$

3. Formation of Structure (B) (cf. Figure 50)

1. Break O=O:	118
2. One C=C goes to one C-C:	65
3. Loss of resonance energy	<u>10.5</u>
Total	193.5
4. Formation of two C=O: $2 \times 170 =$	340

$$\Delta H = 193.5 - 340 = -146.5 \text{ kcal}$$

4. Formation of Structures (C) and (D) (cf. Figure 50)

1. Break O=O:	118
2. Formation of C=O:	170
3. Formation of two (C-O): $2 \times 82 =$	<u>164</u>
Total (2 and 3)	334

$$\Delta H = 118 - 334 = -216 \text{ kcal}$$

5. Formation of Structure (E) (cf. Figure 50)

1. Break O=O:	118
2. One C=C goes to C-C:	65
3. Loss of resonance energy:	<u>10.5</u>
Total	193.5

5. Formation of Structure (E), Continued

4. Formation of two (C-O):	2 x 82 =	164
5. Formation of one (O-O):		<u>39</u>
	Total	203

$$\Delta H = 193.5 - 203 = -9.5 \text{ kcal}$$

10. APPENDIX B

THERMOCHEMISTRY OF CHAR-OXYGEN INTERACTION AT 100°C

A NEW METHOD FOR CHARACTERIZATION OF COAL CHARs

10.1 INTRODUCTION

We have shown the feasibility of using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to study the kinetics and thermochemistry of reactions involved during the interaction of oxygen with Saran chars at selected temperatures in the range 75-850°C. These techniques have then been used to characterize oxygen interaction with coal chars. Results of this study are now presented.

10.2 MATERIALS

Seventeen coal chars were used in the present study. The coals varied in rank from anthracite to lignite. Table B1 presents analyses of the parent coals. The coals were ground and sieved to 40 x 100 mesh and used for preparation of chars. The coals were carbonized in N₂ at 10°C/min up to 1000°C whereafter they were held at this temperature for 2 hr. The chars prepared from strongly caking coals (PSOC-171, 4, and 137) were reground to 40 x 100 mesh. Table B2 presents the ash content and the concentration of the major inorganic elements in the chars.

Selected coals (PSOC-91, 87, 133, 101, and 81) were also washed with 10 volume percent HCl or demineralized (PSOC-87 and 138) with a 1:1 HCl-HF mixture prior to carbonization.

10.3 PROCEDURE

A known weight of char was charged inside the DSC cell or TGA reactor. The sample was outgassed; flushed with N₂ at 45 cc/min, heated up to 600°C, kept at this temperature for 30 min, and finally cooled to room temperature. Following this pretreatment, the char was held isothermally in N₂ at $100 \pm 1.0^\circ\text{C}$ for 45-90 min, to permit

TABLE B2
CONCENTRATION OF INORGANIC IMPURITIES IN THE CHARS

PSOC Char No.	Ash Content, %	Concentration (Expressed as Oxides, %)				
		Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O
89	--	--	--	--	--	--
91	11	0.13	3.77	1.44	0.009	0.032
87	13	0.96	2.73	0.79	0.052	1.50
140	12	1.13	1.35	0.24	0.057	0.067
138	16	1.48	1.30	0.26	0.083	0.077
98	12	1.25	2.27	0.35	0.088	0.029
101	8	0.43	2.67	0.58	0.004	0.053
26	20	12.8	0.97	0.076	0.19	0.052
22	23	2.45	2.05	0.26	0.50	0.080
24	14	3.76	0.14	0.11	0.32	0.043
67	5	1.11	0.85	0.037	0.011	0.11
171	11	2.77	0.68	0.17	0.19	0.18
4	2	0.51	0.12	0.026	0.005	0.039
137	19	9.09	0.24	0.17	0.28	0.047
114	12	0.20	0.098	0.084	0.31	0.041
81	6	0.33	0.14	0.082	0.047	0.010
177	5	0.37	0.04	0.023	0.037	0.033

the attainment of thermal stability of the instruments (invariably smooth horizontal output line). Oxygen was then introduced to replace N_2 at the same flow rate and the thermograms were started. Values of Q (cal/g char) and W (mg/g char) were determined for a 30 min chemisorption time. Values of ΔH (kcal/mole) were also calculated as described in the body of this report.

10.4 RESULTS AND DISCUSSION

10.4.1 Kinetics of Oxygen Chemisorption on Chars

10.4.1.1 Elovich Plots

Dependence of Q (cal/g char) on reaction time is illustrated in Figures B1 and B2. In all cases studied, linearities are observed, thus suggesting that the rate of heat released is exponentially decreasing with (i) increasing weight of oxygen chemisorbed and (ii) increasing Q . Thus

$$(dQ/dt) = a \exp(-\alpha Q)$$

which upon integration is simplified to

$$Q = \frac{2.3}{\alpha} \log a\alpha + \frac{2.3}{\alpha} \log t$$

where

α = constant (g char/cal).

a = initial rate of heat released (cal/g char/min)

Values of α and a are listed in Table B3. As will be shown shortly, values of a may be used to characterize these chars. However, this cannot be generalized. Experience has shown that for some Saran chars subjected to oxygen under rather similar conditions, the Q -log t plots did not conform to one straight line. Instead, there existed one (or more) breaks in the plots, as described in the body of this report. The latter phenomenon was attributed to chemisorption of oxygen on

Figure B 1. Elovich Plots for Coal Chars Exposed to Oxygen at 100°C

Figure B 2. Elovich Plots for Coal Chars Exposed to Oxygen at 100°C

TABLE B3
THE ELOVICH PARAMETERS α AND a FOR COAL CHARs

PSOC Char Number	α (g char/cal)	a (cal/g char/min)
89	0.96	2.04
91	0.53	3.11
87	0.58	2.46
140	1.18	1.81
138	1.15	1.92
98	1.12	1.04
101	0.53	3.46
26	3.07	0.42
22	1.40	0.90
24	1.07	1.37
67	2.04	0.51
171	10.00	0.08
4	3.05	0.24
137	6.58	0.20
114	7.20	0.20
177	7.90	0.09

more than one group of active sites on the Saran surface. Further, for an air-activated Saran char, the W -log t plots were linear up to 200°C. Similar results are reported here for selected coal chars exposed to oxygen at 100°C (cf Figure B3). For some of the chars, the TGA technique was not sufficiently sensitive to measure weight increase due to oxygen chemisorption.

Another approach at characterizing coal chars can be considered. At an arbitrary time, say 15 min, values of heat released, Q_{15} (cal/g char) are considered for the sake of comparison. Plots of Q_{15} versus α are shown in Figure B4. A reasonable linearity is observed. However, owing to the accumulated errors in evaluating values of α , one may rather rely on Q_{15} . Thus, for lignite chars, or the exceptionally reactive PSOC-101 char, the initial rates of heat released are significantly higher than for the remainder of the chars. Values of α are also related to Q_{15} . This is illustrated in Figure B5. As Q_{15} decreases, α is seen to increase asymptotically.

10.4.1.2 Values of ΔH (kcal/mole)

The data presented in Figures B1 and B3 were used to calculate ΔH ($\Delta H = 32Q/W$). For each char, ΔH was almost independent of reaction time thus indicating that gasification reactions were absent. The physical significance of ΔH for oxygen chemisorption on chars and carbonaceous materials is still obscure. In some cases, the magnitude of ΔH may possibly indicate whether the reaction involves only chemisorption or whether physical adsorption is also taking place. Values of ΔH for eight chars studied are listed in Table B4. It is noted that as the carbon content of the parent coal increases, ΔH decreases (in magnitude). One could, therefore, suggest that oxygen

Figure B 3. Dependence of Oxygen Uptake on Reaction Time at 100°C

Figure B 4. Relation between Heat Released (Q_{15}) and the Elovich Parameter (a)

Figure B 5. Relation between Heat Released (Q_{15}) and the Elovich Parameter (α)

TABLE B4
VALUES OF ΔH FOR OXYGEN CHEMISORPTION ON
DIFFERENT COAL CHARs

PSOC Sample Number	Carbon Content of Parent Coal (%, daf)	ΔH (kcal/mole)
89	63.3	82.4
91	70.7	78-79
87	71.2	78
140	71.7	72.8
98	74.3	69-70
101	74.8	69.4
24	80.1	54.5
67	80.4	54.1

atoms are more strongly bonded to chars from low rank coal than those from high rank.

10.4.2 Dependence of Heat Released During Oxygen Chemisorption on Type of Char Used

10.4.2.1 Carbon Content of Parent Coal

Several attempts were made to correlate Q_{15} (cal/g char) to one of the following parameters: (i) carbon content of the parent coals, (ii) ash content of the parent coals, (iii) nitrogen or sulfur content, and (iv) ash content of the chars or each of the major inorganic impurities contained in the chars (cf Table B2). The most meaningful data are shown in Figure B6. As the carbon content of the parent coal increases, from lignites to anthracites, Q_{15} tends generally to decrease. However, for the chars carbonized from high volatile bituminous coals (PSOC-26, 22, 24, 67, and 171), there exists some scatter of the

Figure B 6. Variation of Heat Released with Carbon Content of the Parent Coal

data points. It is remembered (cf Table B1) that for PSOC-26, 22, 24, and 171 coals, the organic sulfur content is high. It is not yet understood whether this sulfur: (i) has a unique effect on the nature of the carbonization process in regard to the structure of the char produced or (ii) inhibits or catalyzes the interaction between chars and oxygen in such a way that values of Q_{15} do not follow one and the same pattern.

10.4.2.2 Nitrogen Surface Area

The relation between Q_{15} and N_2 surface area of chars is shown in Figure B7. As N_2 surface area increases, Q_{15} first increases, passes through a maximum (corresponding to about $62 \text{ m}^2/\text{g}$), and finally decreases. The PSOC-91 char is seen to deviate from the general trend.

10.4.2.3 CO_2 Surface Area

Variation of Q_{15} with CO_2 surface area is indicated by the data points shown in Figure B8. It is known that PSOC-87, 91, and 101 chars are very highly reactive towards gasification reactions. This is also true for oxygen chemisorption on the chars.

10.4.3 Relations between Heat Released during Chemisorption and Rates of Gasification

Dissociative oxygen chemisorption is the first step involved in many gasification reactions. For the chars used in the present study, gasification data (at higher temperatures) were available. These include gasification in air at 405°C (196), in CO_2 at 900°C (197), in steam at 910°C (198), and H_2 at 980°C (199). We have tried to correlate values of Q_{15} (cal/g char) for the chars exposed to oxygen at 100°C with some gasification parameters, for example, R_T and $\tau_{0.5}$, where R_T is the maximum rate of gasification at temperature T , and $\tau_{0.5}$

Figure B 7. Dependence of Q_{15} (cal/g Char) in Nitrogen Surface Area of Chars

Figure B 8. Variation of Q_{15} (cal/g Char) with CO_2 Surface Area

is the time (in minutes) required to gasify 50% of the char. As one might expect, gasification data in H_2 were found to not be related to Q_{15} .

10.4.3.1 Gasification in Air

Two relationships were found: variation in Q_{15} with $R_{40.5}$ (cf Figure B9) and dependence of Q_{15} on $\tau_{0.5}$ (cf Figure B10). As the reactivity of chars increases, Q_{15} increases linearly and then levels off for highly reactive chars. The linearity observed in Figure B10 can now be considered. Let us emphasize first the difference between $R_{40.5}$ and $\tau_{0.5}$. $R_{40.5}$ was calculated (196) by considering the region of maximum slope burn-off versus time plots. This region varied between 0.7 to 4.1% and 10.9 to 50.6% burn-off depending on the char under consideration. However, values of $\tau_{0.5}$ were computed when 50% of the original char was gasified (196).

10.4.3.2 Gasification in Steam and in CO_2

Dependence of Q_{15} on $\tau_{0.5}$ is shown in Figures B11 and B12 for gasification in steam and CO_2 , respectively. Here the relation is no longer linear. Instead, Q_{15} sharply decreases with $\tau_{0.5}$ for highly reactive chars and finally levels off.

10.4.4 Effect of Mineral Matter on Q

Removal of mineral matter from the parent coal by acid washing (AW) or by demineralizing (DEM) prior to carbonization has a marked effect on values of Q . Elovich plots for these chars are shown in Figure B13. It is believed at this stage that more char samples have to be investigated before a firm conclusion could be reached. However, a few general observations can be made. These are: (i) for AW lignite chars (PSOC-91, 87, and 138), values of Q at most time intervals are

Figure B 9. Relation between Reactivities of Chars in Air at 405 °C and the Heats Released in Oxygen at 100 °C

Figure B 10. Variation of Q_{15} with Time Required to Gasify 50% of Chars in Air

Figure B 11. Variation of Q_{15} in Oxygen at 100°C with $\tau_{0.5}$ in Steam at 910°C

Figure B 12. Variation of Q_{15} in Oxygen at 100°C with $\tau_{0.5}$ in CO_2 at 900°C

Figure B 13. Elovich Plots for Acid Washed and Demineralized Coal Chars

essentially the same; (ii) for an anthracite char (PSOC-81), the Q-t plot is essentially the same for the raw or AW char; and (iii) for DEM chars, values Q_{15} are lower than those obtained for the original chars.

Table B5 summarizes the data and some experimental parameters obtained with five different AW or DEM chars. It is noted that removal of mineral matter from the precursor coals has a more pronounced effect on decreasing gasification rates than chemisorption rates when the chars are exposed to oxygen.

TABLE B5
SURFACE AREAS AND REACTIVITY PARAMETERS
FOR ACID WASHED AND DEMINERALIZED COAL CHARs

PSOC Sample Number	Ash, %	Surface Areas (m ² /g)		R_{405}^* (g hr ⁻¹ g ⁻¹)	Q_{15}^{**} (cal/g)
		N ₂	CO ₂		
91	10.9	35	471	2.70	6.13
91 AW	1.3	89	924	0.12	3.07
87	13.1	107	299	1.10	5.28
87 AW	2.6	11	626	0.31	3.17
87 DEM	0.0	1	600	0.23	4.08
138	16.0	143	667	0.53	3.04
138 AW	9.6	4	752	0.31	3.27
138 DEM	0.9	47	116	0.17	0.64
101	8.2	68	501	1.84	6.04
101 AW	1.1	3	667	0.20	2.14
81	6.4	1	42	0.11	0.38
81 AW	5.8	<1	42	0.16	0.38

* in air

** in oxygen