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THE USE OF PARTIAL-PRESSURE MASS SPECTROMETRY IN THE THERMAL ANALYSIS STUDY OF CARBONS AND GRAPHITE

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ABSTRACT

A versatile partial-pressure mass spectrometer system is described for measuring gaseous species thermally desorbed from solid surfaces. The system evaluates not only the ratio of masses present in the gaseous phase but also the specific mass (mg/g of solid) desorbed or decomposed during thermal treatment. The extension of the method to oxidation studies is also described.

A study has been made of the evolution of gases from graphitic and non-graphitic carbons. These range in properties from a non-graphitic carbon, a PVDC charcoal of molecular sieve type, through a ground graphite of specific surface 102 m^2/g to a nuclear type graphite of 0.6 m^2/g.

The formation of surface oxide on a clean surface at pressures of the order 0.2 mm Hg is evaluated along with the subsequent thermal decomposition of the surface oxide. The data from this paper together with other published work on graphites is used to illustrate the application of the thermal-desorption results to oxidation studies on carbons and graphites.

INTRODUCTION

The reaction of molecular oxygen with graphite is primarily associated with the peripheral atoms of the basal planes[1]. Graphite-oxygen reactivity is therefore closely related to the extent of the graphite edge planes (see Results: A graphitic carbon, p. 504). Low-temperature oxidation of graphites at temperatures below 1000°C is markedly influenced by the presence of stable surface oxide[2].

It has now been established that the oxidation of graphite proceeds[3] by the formation of stable surface oxide and the production of gaseous CO and CO_2. At a given temperature the reaction between oxygen and a clean graphite surface has an initial transient period of surface oxide formation followed by a steady state reaction of the oxygen with the remaining uncovered part of the reactive surface. The steady state rate of oxidation is thus dependent on the proportion of exposed reactive surface.

The above mechanism has led us to investigate the proportion of the total surface which can be covered with surface oxide and the stability of the oxide as a function of temperature. The use of a partial-pressure mass spectrometer allows us to follow the formation of surface oxide during the transient period of oxidation. The subsequent thermal decomposition of the surface oxide can also be followed, and this permits the measurement of the extent and thermal stability of the surface oxide, leading to an insight into the heterogeneous nature of the reactive surface[4].

EXPERIMENTAL

Apparatus

The apparatus employed (Fig. 1) was a static reaction system which consisted basically of a 40-cc high-purity silica reaction chamber leading into a 5.5-litre reservoir. The reservoir was connected to an AEI MS10 mass spectrometer *via* a fixed 10-lusec molecular leak valve, which allowed partial pressures of 0.1–600 microns in the reservoir to be measured with 1% accuracy on the mass spectrometer. The MS10 is a 2" radius, 180° deflection instrument employing electrostatic scanning. The mass-spectrometer pumping system consisted of a 3" oil diffusion pump, cold trap and an orifice plate with a 1-litre/sec conductance. This arrangement allows continuous monitoring of the gaseous components in the reservoir with a sample loss of less than 2% over a period of 1 h. A calibrated McLeod gauge was used to obtain conversion factors for ion current readings of CO, CO_2, and O_2 *etc.* on the mass spectrometer to partial pressures in the reservoir chamber. Typical sensitivity-calibration plots are shown in Fig. 2, which are obtained at the beginning and end of each experimental run. The reaction chamber and the reservoir could be evacuated to 10^{-6} mm Hg using two cold traps and an oil diffusion pump. High-vacuum PTFE greaseless stopcocks were employed throughout the reaction system. A Cahn microbalance could be used in conjunction with the MS10 mass spectrometer.

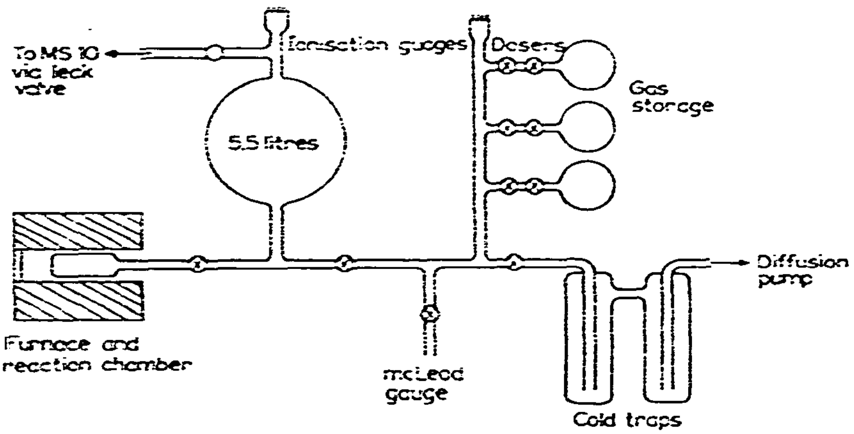

Fig. 1. Sorption–desorption apparatus.

Design considerations

The present experimental arrangement is based on experience gained from the use of, and interpretation of results obtained on, a previous design[5] which employed a

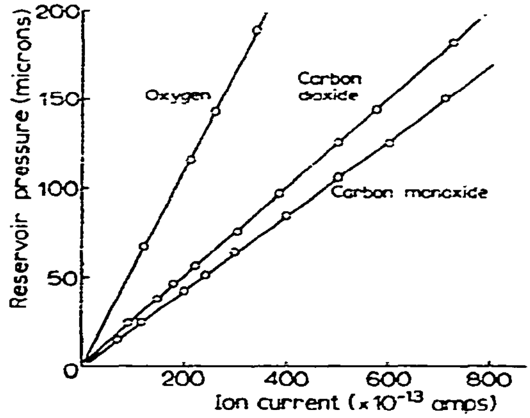

Fig. 2. Typical calibration curves showing the relation between ion current in the mass spectrometer and the pressure in the reservoir.

'batch'-type sampling system. Certain disadvantages of a 'batch' sampling system were encountered for this type of investigation.

a. — The secondary reactions occurring between gaseous products and the sample when accumulating them over the sample.

b. — The procedure of taking doses for analysis leads to a complicated mathematical correction[5] to obtain quantitative results.

c. — When the majority of the evolved gas is contained in the reaction chamber a large correction is necessary to allow for the difference in gas density in the hot and cold reaction zones[5].

d. — The inability of the system to monitor a continuous process.

The present system employs a direct sampling technique in which the majority of the evolved gas is collected in a 5.5-litre reservoir. The correction for about 30 cc of the gas in the hot reaction zone is negligible relative to large reservoir volume. By a method employing an incremental desorption programme the problem of secondary gaseous reactions is reduced to a minimum by removing the desorbed gas at the temperature of desorption (*cf.*: General procedure, below). This system allows direct monitoring of the reaction process, provided some consideration is given to the mass of the sample and the extent of the gas evolution.

General procedure

The graphitic and non-graphitic samples were first cleaned by evacuating them to 10^{-6} mm Hg for 3 h at 950°C. After cooling to the reaction temperature, the sample was isolated in the reaction chamber and a pre-determined oxygen pressure set in the reservoir. Initial pressures of oxygen were measured with the McLeod gauge and on exposing the sample to the oxygen, the increase in the 28 (CO^+) and 44 (CO_2^+) mass peaks and the decrease in the 32 (O_2^+) mass peak were monitored with time. The depletion of oxygen in the gas phase gives the amount of surface oxide formed. At the end of an oxidation the oxygen and 'burn off' products above the sample were removed by evacuation. The reaction chamber and reservoir were isolated from the diffusion pump and the sample temperature raised in given increments. During desorption studies the evolved CO and CO_2 resulting from the decomposition of surface oxide were monitored with time. At the end of each desorption run the reaction chamber was isolated from the reservoir, which was then quickly evacuated. This method prevented loss by isothermal desorption of the surface oxide during evacuation. Once evacuated the reservoir and reaction chamber were re-connected and the residual gas in the reaction chamber allowed to expand into the reservoir. This contribution to the reservoir background was usually found to be small and could easily be corrected for. By accurately calibrating the volume of the reservoir and by using the General Gas Law, $PV = mRT$, the mass of evolved gas at each stage could be determined.

RESULTS

Non-graphitic carbon

This material was a polyvinylidene chloride carbon[6] which has been the subject of a recent study. The versatility of the present system is illustrated in part by Fig. 3 which shows the progressive formation of surface oxide on the clean surface of the PVDC carbon of total specific surface 1000 m^2/g. Also shown is the accompanying depletion of oxygen and the production of 'burn off' products CO and CO_2. The amount of chemisorbed oxygen can be obtained directly from Fig. 3 or by subsequent decomposition of the surface oxide and analysis of the oxygen present in the CO and CO_2 gaseous products (Fig. 4).

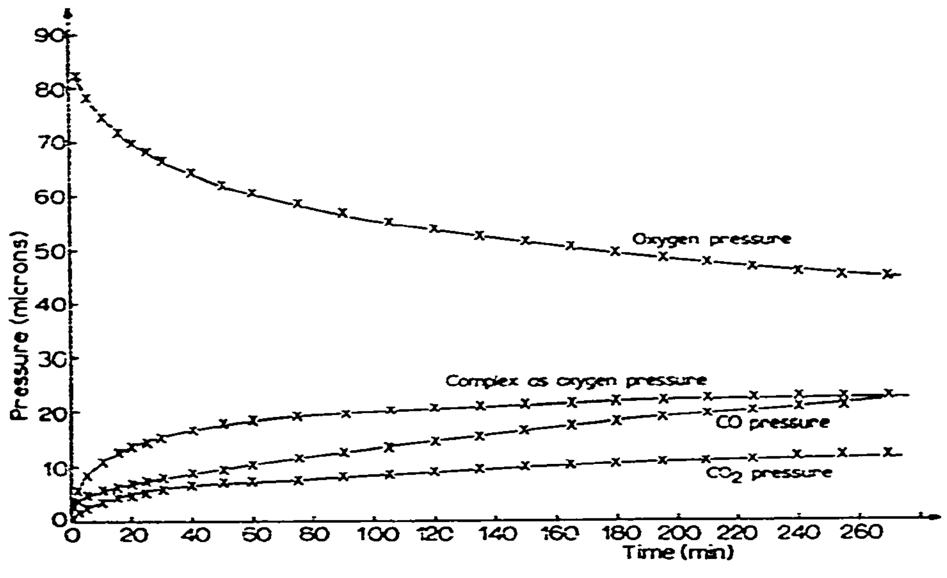

Fig. 3. Oxygen chemisorption on PVDC carbon.

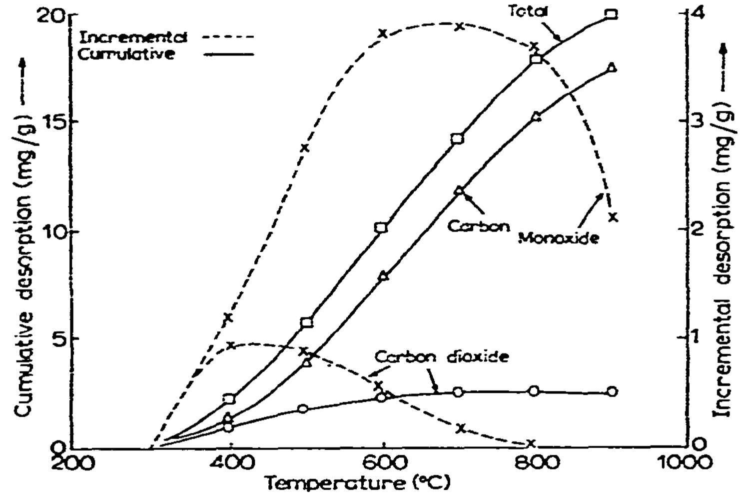

Fig. 4. Desorption of gaseous species from PVDC carbon.

The extent of surface oxide coverage can be determined from the number of carbon atoms desorbed on the basis of an assigned cross sectional area of 8.3 $Å^2$ for a carbon atom on the edge plane of graphite. The extent of surface oxide coverage on this non-graphitic carbon was found to be about 30 m^2/g or about 3% of the total surface.

The technique of isothermal desorption of the surface oxide can yield valuable information as to the energetic nature of the oxide on the surface. By using the isothermal pressure *vs.* time curves it is possible to obtain accurate isothermal desorption-rate data. A computer programme has been developed which will fit each curve to an *n*th degree polynomial obtaining the best fit. Plots of log (desorption rate) *vs.* total amount desorbed yield straight lines corresponding to each incremental desorption range.

From these plots it is possible to obtain two values for the rate of desorption at two consecutive temperature increments, both rates corresponding to one value of surface coverage. The activation energy of desorption (E) is then given by:

$$\log\left(\frac{\text{desorption rate at } T_2}{\text{desorption rate at } T_1}\right) = \frac{E}{2.3\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where R is the gas constant.

Fig. 5 shows a typical plot of log (desorption rate) *vs.* amount desorbed for CO desorbed from the PVDC carbon. The results obtained for the relationship between the activation energy of desorption and surface coverage of CO is shown in Fig. 6 for two successive chemisorption–desorption cycles. This type of result might well be expected for an active carbon. These carbons are adsorbents with energy-heterogeneous surfaces resulting from both the random arrangement of elementary carbon crystallites on the surface of the adsorbent and the effect of the increase in energy of adsorption in very fine pores of carbon due to the superposition of forces of the opposite capillary walls[7].

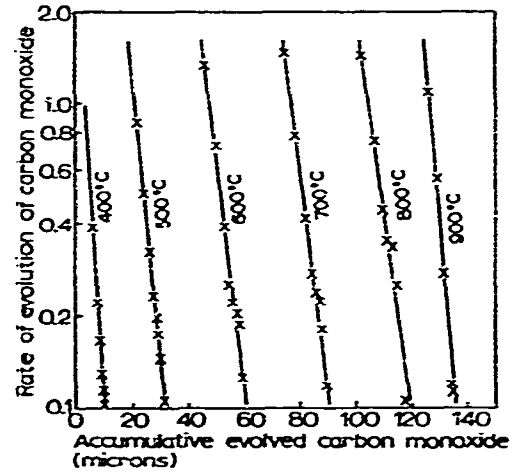

Fig. 5. Logarithmic desorption graphs for PVDC carbon, for activation-energy determination.

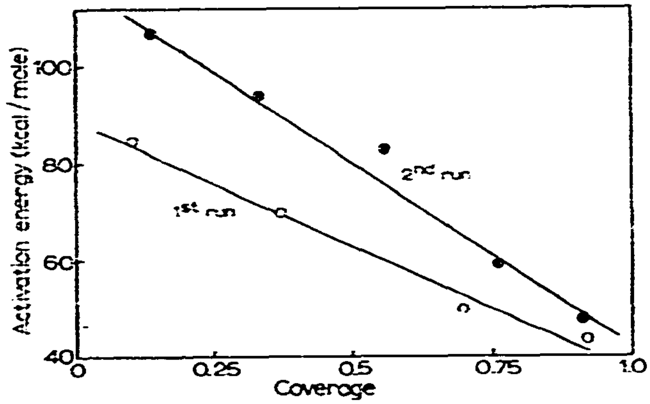

Fig. 6. Activation-energy variations for PVDC carbon.

A graphitic carbon

This material was a ground Acheson's graphite with a total surface area, found by gas-adsorption methods, of 102 m^2/g.

Graphite is a crystalline material, belonging to the hexagonal crystal system, in which sheets of carbon atoms, arranged in hexagonal array, are stacked parallel to one another in a specific orientation. A graphite crystal can therefore be seen to have two kinds of surface, namely the sheets of carbon atoms which are called basal planes, and planes or surfaces perpendicular to the sheets which are called edge planes. Since the carbon–oxygen reaction is concerned with the peripheral atoms of the basal planes[1] the important surface area is the edge plane area.

A measure of this area and of that of the basal plane can be obtained from a study of the widths of the lines in an X-ray powder diffraction pattern of the graphite sample[11]. The width, at half peak height, β, of the line produced by the reflection of X-rays from a particular family of lattice planes in the crystal is related to the size of the crystal measured perpendicular to those planes, t, by the equation

$$\beta = \frac{0.9\,\lambda}{t\cos\theta}$$

where λ is the wavelength of the X-rays and θ is the glancing angle of incidence of the X-rays on the family of lattice planes. To use this equation β has to be corrected for the 'instrumental width', *i.e.* the minimum width of line that can be obtained for any sample. Hence measurement of the widths of lines of indices $00l$ and $hk0$ will give the size of the crystals perpendicular and parallel, respectively, to the basal planes. Knowing the density of the graphite one can then calculate the specific surface area of the basal and of the edge planes, and of course the total specific surface area.

Powder photographs of the graphite samples were obtained using a quadruple Guinier focussing camera and the profiles of the lines were obtained using a recording microdensitometer. The profiles of the 004 and 110 lines were examined and the line widths determined. Assuming the ideal graphite density, since the X-ray method measures the extent of the regions of perfect crystallinity, it was found that the total surface area of the Acheson's graphite was about 100 m^2/g and the specific edge plane area was about 46 m^2/g.

A series of experiments have been carried out on the cleaned surface of this graphite over a range of increasing temperatures. The interaction of oxygen at 300 and 400 °C is illustrated in Fig. 7. Graphs of the type shown in Fig. 7 show the relationship between the various gaseous products during the course of an oxidation. However, for a more detailed insight into the rate controlling mechanism for the oxidation it is necessary to plot graphs similar to Fig. 8 where the log of oxygen pressure is plotted against time.

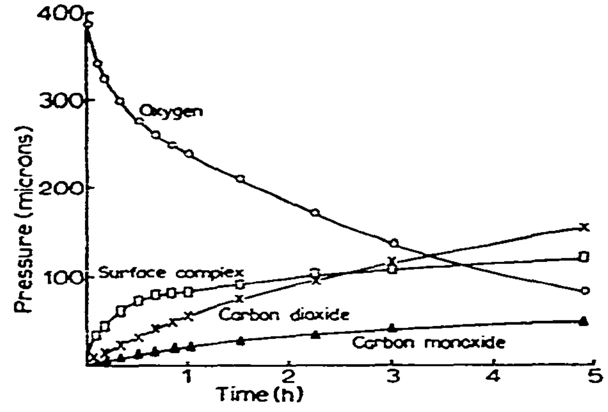

Fig. 7. Oxygen chemisorption on Acheson's graphite.

The straight lines obtained indicate that there is a 1st order reaction where the rate controlling process is the dissociation of the oxygen molecule at the graphite surface. The initial deviations from a 1st order reaction are illustrated in the 300 and

400°C oxidation graphs and are due to the extra depletion of oxygen pressure to form the surface oxide in the initial transient period.

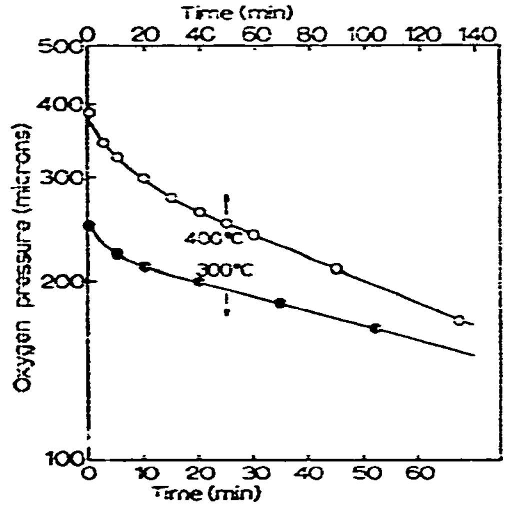

Fig. 8. Oxygen chemisorption on Acheson's graphite: logarithmic graphs.

Nuclear-type graphite

This was an improved nuclear-type graphite with a total specific surface of 0.62 m^2/g obtained by low-temperature krypton adsorption and showing the characteristic stepped adsorption isotherms of graphites. The X-ray method, however, gave a total specific surface area of the order of 100 m^2/g of which about half is edge plane area. It is interesting to show how the present system can be used to study the initial degassing of such a low-surface area material. Tables I and II show the masses of evolved species desorbed from the surface during the initial degassing and after exposure to the atmosphere for 15 days.

Using 10 g of sample, sensitivities down to 0.01 μg have been obtained which compare favourably with the most advanced microbalances. The extent of surface oxide coverage after atmospheric exposure was 0.099 and 0.037 m^2/g before and after treatment to 950°C, respectively.

DISCUSSION

The application of mass spectrometry to the study of carbon and graphite reactivity has provided a technique for studying the fundamental processes involved at the surface of a wide range of these materials. The present system allows adsorption–desorption phenomena to be studied with at least the same accuracy as given by a conventional microbalance but yielding far more discriminate information. The weight changes involved, if these processes were monitored thermogravimetrically, would be a complex function of at least two independent processes. Both the weight increase due to chemisorption of oxygen to produce surface oxide and the weight loss due to the removal of carbon atoms as CO and CO_2 are contributing to

TABLE I

CUMULATIVE THERMAL DESORPTION FROM ORIGINAL NUCLEAR GRAPHITE[a]

Temperature range (°C)	H_2	CO	CO_2	H_2O	N_2	*Hydrocarbons*
0–200	0.04	0.57	5.66	1.08	1.58	0.31
0–400	0.10	6.75	14.98	2.45	5.33	1.12
0–600	0.55	8.25	48.69	2.45	7.62	2.01
0–800	1.27	14.74	54.19	2.45	8.09	2.01
0–900	1.78	20.12	56.34	2.45	8.66	2.01

[a]Quantities expressed in $\mu g/g$ of sample.

TABLE II

CUMULATIVE THERMAL DESORPTION FROM NUCLEAR GRAPHITE PRE-DEGASSED AT 950 °C FOR 3 H AND EXPOSED TO ATMOSPHERE FOR 15 DAYS[a]

Temperature range (°C)	H_2	CO	CO_2	H_2O	N_2	*Hydrocarbons*
0–200	—	—	—	—	—	—
0–300	—	—	—	—	—	—
0–400	0.01	0.21	0.51	0.18	0.42	0.06
0–600	0.02	1.67	21.97	0.43	0.62	0.13
0–800	0.10	3.71	23.52	0.51	0.82	0.16
0–900	0.22	6.13	23.52	0.51	0.91	0.16

[a]Quantities expressed in $\mu g/g$ of sample.

the net measured weight change. Normally in thermogravimetric studies this period is by-passed and the process is monitored after the steady state has been reached where only the gaseous products CO and CO_2 are being formed. With the mass spectrometer system the initial transient period can be broken down into the various competing processes. It is hoped that a detailed study of the transient period will lead to more fundamental ideas about the relevant mechanisms. The direct monitoring of oxidation at different temperatures can be seen to produce varying ratios of CO and CO_2. These can be easily followed with the aid of a mass spectrometer and compared with those ratios that are predicted by theoretical thermodynamic considerations.

The combined use of a mass spectrometer and microbalance has provided a direct correlation between the two methods of study for the desorbed species from graphite[8]. A direct agreement has been obtained by using the two methods simultaneously. The present system described in this paper has been developed for the study of much smaller surface area materials than usually examined by using a variable leak valve and ultra high-vacuum components. In the range of pressures which the system normally encounters, degassing from the walls and leaks are relatively undetectable, but development of the system to work at pressures below 10^{-5} mm Hg requires a careful evaluation of leak rates, degassing and adsorption onto the walls.

In more conventional thermal-analysis studies these problems are less severe in that the gas evolution on decomposition is far greater than the small amounts evolved from a nuclear-type graphite.

An interesting comment on the results obtained for the nuclear graphite is provided by the X-ray determination of surface area for this material. The surface areas are of the same order as those for the Acheson's graphite and are therefore considerably greater than the gas-adsorption value and the area of surface oxygen coverage. It follows that these low values cannot be due to this graphite having large crystals. The X-ray measurements show that the crystals are small. We must therefore conclude that their surfaces are inaccessible to the gas phase, since they are not measured by the gas-adsorption method. This interpretation is confirmed to a large extent by subsequent work on this nuclear graphite which shows that the carbon–oxygen reactions are diffusion controlled[10], *i.e.* that the rates of reaction are controlled by surface migration or diffusion rather than by surface reactivity.

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