

## Hydrophilic Oxygen Complexes on Activated Graphon

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Graphon samples have been reacted in air at 500°C to different carbon burn-offs up to 70% in order to produce samples of varying active surface areas. The extent of active surface area developed was measured by oxygen chemisorption at 350°C. It increased from 0.2 to a maximum of 5.2 m<sup>2</sup>/gm with increasing carbon burn-off up to 70%. In all cases the active area was less than 4% of the BET area, measured by N<sub>2</sub> at 78°K. Adsorption of water on the activated samples, having their active sites partially or completely covered by oxygen complex, was studied between -3.3° and 20°C. The amount of water adsorbed was shown to be proportional to the area covered by oxygen. Adsorption was reversible at relative pressures below 0.4. The heat of adsorption of water over essentially all the monolayer region closely approached its heat of liquefaction; in this case completion of monolayer coverage with water occurs at  $p/p_0 = 0.5$ . With the area of the water molecule taken to be 10.6 Å<sup>2</sup>, which is the value calculated for hexagonal close packing, excellent agreement was found between the water adsorption area and the area covered by oxygen chemisorption.

### I. INTRODUCTION

A number of studies have been conducted on water adsorption on carbon surfaces. These studies have all led to the same qualitative conclusions: (1) well-cleaned carbon surfaces are essentially hydrophobic, and (2) the presence of oxygen complexes on some fraction of the surface renders that surface hydrophilic. Carbons studied include charcoal (1-4), raw carbon blacks (3-6), graphitized carbon blacks (4, 6-8), natural graphite (9), nuclear graphite (10), and graphite wear dust (11).

Zettlemoyer and co-workers (7) studied water adsorption between 10° and 25°C on the graphitized carbon black, Graphon. They cleaned their sample at 400°C for 12 hours at 10<sup>-5</sup> torr before making adsorption measurements. They concluded that water adsorbed in clusters on only 1/1500 of the total Graphon surface. Healey and co-workers (8) modified the Graphon surface by oxidizing it in 1 atm of O<sub>2</sub> at 530°C for various times up to 17 hours. The oxidized samples were degassed at 10<sup>-5</sup> torr at room temperature prior to the study of water adsorption at 25°C. Undoubtedly this treat-

ment both gasified away some carbon (thereby partially activating the Graphon) and formed some oxygen complex on the carbon surface, which was not removed by degassing at room temperature (12). The authors, however, did not measure the extent of carbon burn-off nor the amount of oxygen complex formed; but it is expected that the fraction of surface covered with complex would have increased with increasing oxidation time. Healey and co-workers showed that increasing oxidation caused a progressive increase in water adsorbed at all relative pressures studied (i.e., up to 0.6). The authors reported surface areas calculated from BET plots of water adsorption (which they say showed considerable scatter), which sharply increased with increasing Graphon oxidation. When the isotherms were plotted as fraction of hydrophilic surface covered by water versus relative pressure, all isotherms fell on a single curve. On this basis, it was concluded that water adsorption on oxidized Graphon was occurring by a clustering around hydrophilic sites, where these sites were not isolated and randomly scattered about the surface but rather grouped

together in patches, perhaps at the edges of the graphitic planes. Following oxidation for the maximum time of 17 hours, the fraction of the total Graphon surface which adsorbed water was 0.124.

Essentially, our study is an extension of the previous study of Healey and co-workers, where we have attempted to relate quantitatively the area occupied by oxygen complexes on Graphon surfaces to the area subsequently occupied by physically adsorbed water.

## II. EXPERIMENTAL

*A. Adsorption Apparatus.* Adsorption was measured gravimetrically with the use of a helical quartz spring, 7–8 mm in diameter and 500 turns, having a capacity of 500 mg. At 25°C, the spring constant was 2.02 mm/mg. To avoid detectable variations in this constant, the room (and spring) were maintained at  $25^\circ \pm 0.1^\circ\text{C}$ . To assure that the spring remained at  $25^\circ \pm 0.1^\circ\text{C}$  during adsorption measurements, sample buckets were suspended from a 15 cm long intermediate Vycor hook. Such an arrangement also permitted degassing of samples up to 1000°C, without damaging the spring. After the connecting hook and quartz sample bucket were attached, the maximum weight of sample which could be used was about 300 mg.

The spring was enclosed in a tube 150 cm in length and 3.5 cm in diameter. The upper portion of the tube was Pyrex, and the lower portion was made of quartz. The remainder of the glass apparatus was of conventional vacuum design.

Spring extensions (or weight changes) were measured with a Griffin and George cathetometer. A minimum weight change of about  $5 \times 10^{-6}$  gm could be detected; but because of small fluctuations in spring temperature ( $\pm 0.1^\circ\text{C}$ ), weight changes could be measured accurately only to  $2 \times 10^{-5}$  gm.

Adsorption temperatures between  $-3.3^\circ$  and  $20^\circ\text{C}$  could be maintained within  $\pm 0.1^\circ\text{C}$  by surrounding the lower portion of the sample tube with a 50 cm Dewar through which water or water-antifreeze mixture (at the appropriate temperature) was continuously circulated.

Most of the desired vapor pressures of water were generated by immersing a bulb of

water in a Forma temperature bath (containing appropriate water-antifreeze mixtures) controlled to  $\pm 0.02^\circ\text{C}$ . Water temperature inside the bulb was measured using a copper-constantan thermocouple located inside a well submerged in the adsorption water. From the water temperature, its pressure was obtained from standard reference tables. It was estimated that the transition point from supercooled liquid water to ice occurred at about  $-8^\circ\text{C}$ . For the lower temperature isotherms, it was necessary to use ice down to  $-40^\circ\text{C}$  to generate the lower vapor pressures of water required. Since the Forma unit did not cool below  $-20^\circ\text{C}$ , lower bath temperatures were generated by using various mixtures of ethyl alcohol and water, cooled by liquid  $\text{N}_2$ . Temperatures could be maintained within  $\pm 0.5^\circ\text{C}$  for desired periods.

*B. Materials Used.* The carbon used in the experiments was graphitized Spheron-6 carbon black, Graphon, supplied by the Cabot Corporation. It came from batch D-5 heated to about  $2800^\circ\text{C}$ . From  $\text{N}_2$  adsorption at 78°K, a BET surface area of 82 m<sup>2</sup>/gm was calculated. Graphon was chosen for this study because its particles are nonporous and it has a small degree of surface heterogeneity (13), which can be conveniently increased by carbon gasification (12). The total impurity content was estimated, by emission spectroscopy, to be  $< 15$  ppm.

The  $\text{O}_2$  used for chemisorption was extra dry grade of at least 99.6% purity from the Matheson Corporation. The water used for adsorption was triply distilled ("demineralized") water from Lemont Scientific Co. It was further purified of dissolved gas by repeated cycles of freezing, out-gassing, and melting.

*C. Experimental Procedure.* Samples of original Graphon (held in silica boats) were oxidized at  $500^\circ\text{C}$  in a stream of 1 atm of dry air for periods up to 500 hours to produce desired degrees of activation. The rate of burn-off of Graphon was found to be independent of bed depths up to 1 inch, which means that oxidation was performed at a sufficiently slow rate to assure uniform gasification through the carbon bed (14). Following oxidation, the samples were heated to  $950^\circ\text{C}$  and held for 1 hour in a flowing

high-purity  $N_2$  stream to desorb most of the surface oxygen complexes in the form of CO and  $CO_2$ . After a sample was placed in a quartz bucket and located in the adsorption apparatus, it was further cleaned by heating to  $950^\circ C$  for 12 hours in a vacuum of  $10^{-5}$  torr.

Where desired, the Graphon samples were then saturated with a surface oxygen complex by exposing them to 0.5 torr of  $O_2$  at  $350^\circ C$  for 24 hours. Kinetic studies have shown that saturation of the surface is essentially complete under these conditions (15). The residual  $O_2$  atmosphere was then pumped from the system at  $350^\circ C$  and the sample cooled to room temperature. The amount of oxygen complex introduced in this way could not be weighed directly, because about 0.1 mg of the carbon sample (in a total sample weight of about 300 mg) was gasified under the conditions used. Rather, the amount of oxygen chemisorbed was determined by heating the sample to  $950^\circ C$  under a vacuum of  $10^{-5}$  torr and measuring its decrease in weight. Previous studies have shown that essentially all the oxygen chemisorbed at  $350^\circ C$  can be removed under this condition (12). This loss of weight was converted to weight of oxygen removed, on the assumption that almost all the oxides of carbon came off as CO (12). Repeated runs showed that the amount of oxygen chemisorbed at  $350^\circ C$  remained constant under the adsorption conditions used and that slight gasification did not alter the surface significantly.

If it was desired to remove only a portion of the oxygen chemisorbed at  $350^\circ C$ , the sample was degassed at some intermediate temperature between  $350^\circ$  and  $950^\circ C$ . It was found that this method of producing variable coverage of active sites with oxygen was reproducible.

Before making adsorption runs it was confirmed that no corrections to the measurements had to be made because of: (1) water adsorption on the sample bucket and spring or (2) buoyancy in the pressure range of interest (i.e., up to 17 torr).

Water adsorption was measured at temperatures between  $-3.3^\circ$  and  $20^\circ C$ . An adsorption time of 30 min was used for each isotherm point once the bath determining

TABLE I  
ACTIVATION OF GRAPHON

Burn-Off (%)	Surface area ( $m^2/gm$ )		% ASA of BET area
	BET	ASA	
0.0	82	0.2	0.2
9.1	92	1.9	2.1
24.9	115	3.9	3.4
37.9	128	4.9	3.8
70.4	135	5.2	3.9

the pressure of water had reached the desired temperature. Equilibration was attained in all cases within 30 min.

Desorption isotherms were reversible at relative pressures below about 0.5, and thus successive isotherms could be measured at various temperatures without the requirement of first degassing at higher temperatures.

### III. RESULTS AND DISCUSSION

*A. Activation of Graphon.* Table I summarizes results for the increase in BET and active surface area (ASA) of Graphon with burn-off in air at  $500^\circ C$ . BET areas were calculated from  $N_2$  adsorption isotherms measured at  $78^\circ K$ , with the area of the  $N_2$  molecule taken as  $16.2 \text{ \AA}^2$ . ASA values were calculated from oxygen chemisorption at  $350^\circ C$ , the amount chemisorbed determined as just described. It has been shown that oxygen chemisorbs on the edges of the graphite crystallites, i.e., on carbon atoms located on the (10 $\bar{1}$ ) and (11 $\bar{2}$ ) planes (16). Carbon atoms in these planes occupy an area of *ca.*  $8.3 \text{ \AA}^2$ . Since chemisorption of oxygen is known to be dissociative (17), it is assumed that one oxygen atom chemisorbs on each carbon atom and thus also occupies an area of  $8.3 \text{ \AA}^2$ . As shown previously (12), activation of Graphon produced a minor increase in total surface area but a major increase in active area. Upon 70.4% burn-off, the total area increased only 1.6-fold but the active area increased about 25-fold. Even following 70.4% burn-off, however, the area active to forming a surface oxygen complex was less than 4% of the total surface area.

*B. Water Adsorption on Graphon Where the ASA Is Saturated with Oxygen Complex.* Figure 1 presents isotherms for water adsorption at  $20^\circ C$  on samples of Graphon of

different degrees of activation, where the ASA is saturated with oxygen complex. As expected, water adsorption increased as activation of the Graphon was increased, most of the increase occurring, however, in the first 25% carbon burn-off. In Fig. 2, the adsorption data are normalized, expressing water adsorption per unit of surface area covered by oxygen complex (taken from Table I). It is clear from Fig. 2 that the extent of water adsorption is at least proportional to that fraction of the Graphon surface covered by chemisorbed oxygen.

*C. Desorption Isotherms.* In all cases studied, adsorption-desorption branches of the isotherms coincided at relative pressures below at least 0.4. At higher relative pressures, however, hysteresis was always noted. Figure 3 presents typical isotherms for water sorption at 20°C on the fully oxygen-covered surface of Graphon previously activated to 37.9% burn-off.

Puri (18) measured water sorption isotherms on a sugar charcoal, which had been outgassed at various temperatures up to 1000°C. He showed that the adsorption-

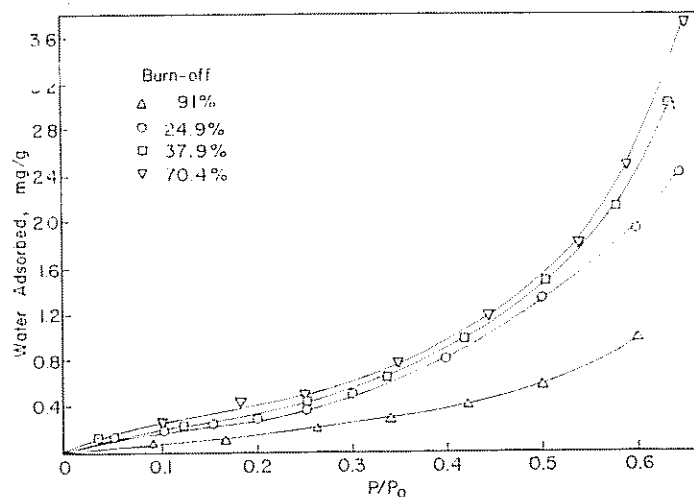


FIG. 1. Water adsorption at 20°C on Graphon samples of different degrees of activation. The active surface areas were saturated with oxygen complex.

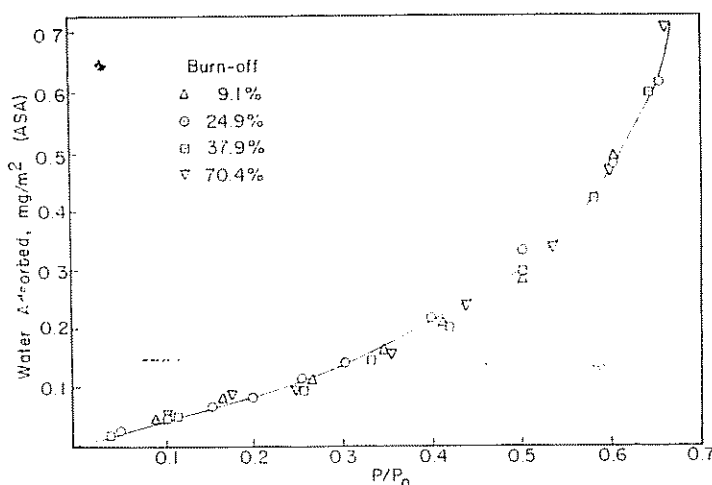


FIG. 2. Water adsorption at 20°C on Graphon samples of different degrees of activation. The amount adsorbed is normalized on a basis of active surface area covered by oxygen complex.

desorption isotherms do not meet, even close to zero relative pressure, as long as oxygen complex is present on the charcoal surface, which can be removed at higher temperatures as  $\text{CO}_2$ . Closure of the hysteresis loop at a relative pressure of 0.2 for the charcoal sample outgassed at  $750^\circ\text{C}$  coincided with the complete removal of all  $\text{CO}_2$ -producing complex. Puri suggested that this complex may be carboxyl and/or lactone groups. As discussed previously, little  $\text{CO}_2$  is produced upon degassing the complex put on Graphon at  $350^\circ\text{C}$  in the presence of extra dry  $\text{O}_2$  (12). Thus, our results appear to be consistent with Puri's findings, even though the two carbons have significant differences in crystallite size and impurity concentrations. It has previously been suggested that oxygen complex which decomposes to produce  $\text{CO}$  is in the form of carbonyl groups (16, 19).

Kiselev and co-workers (11) have recently studied the sorption of water on graphite wear dust, which was first exposed to  $\text{O}_2$  at  $20^\circ\text{C}$ . Isotherms did not close down to low relative pressures of water, but this coincided with heats of adsorption at low pressures of up to four times the heat of liquefaction of water. The authors showed that the water had interacted with the oxygen complexes to form carboxyl and phenolic groups; presumably the reaction was catalyzed by highly dispersed iron contaminat-

ing the samples as a result of the grinding operation.

*D. Heat of Water Adsorption on Graphon.* The heat of adsorption of water on the 37.9% burn-off Graphon, the surface of which was saturated with oxygen at  $350^\circ\text{C}$ , was calculated from isotherms measured at  $20.0^\circ$ ,  $10.0^\circ$ ,  $1.0^\circ$ , and  $-3.3^\circ\text{C}$ . The adsorption isotherms are shown in Fig. 4. When the data are plotted on a relative pressure basis, as in Fig. 5, all isotherms closely coincide over the relative pressure range from 0.02 to 0.63. This means that the isosteric heat of adsorption of water over the temperature and relative pressure range covered closely approached the value for the heat of liquefaction of water, i.e., 10.6 kcal/mole. Pierce and Smith previously showed that the net heat of adsorption of water on Graphon cleaned at  $1100^\circ\text{C}$  was zero between  $0^\circ\text{C}$  and  $28.6^\circ\text{C}$  up to a relative pressure of 0.9 (20).

*E. Surface Areas Calculated from Water Adsorption on Graphon Surfaces Saturated with Oxygen Complex.* It is, of course, of great interest to compare the surface areas calculated from oxygen chemisorption results with those calculated from the physical adsorption of water on Graphon covered with chemisorbed oxygen. Consider the use of the BET equation which is given as

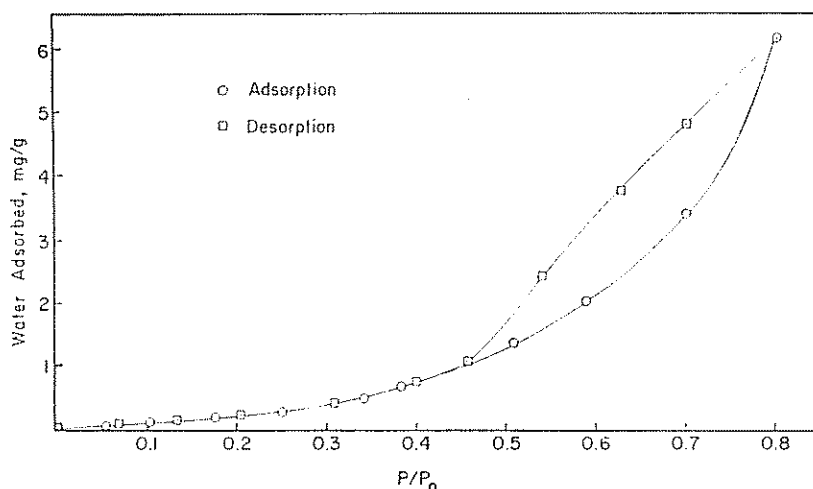


Fig. 3. Water adsorption-desorption isotherms at  $20^\circ\text{C}$  on Graphon activated to 37.9% burn-off. The active surface area was covered with oxygen complex.

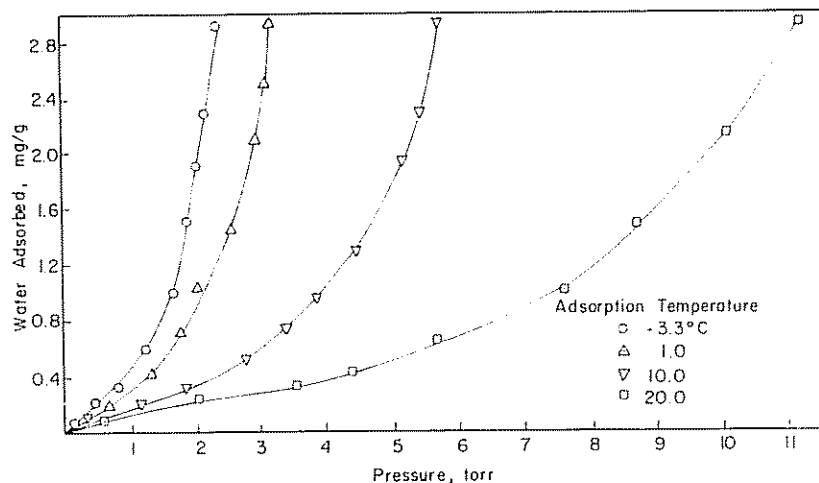


FIG. 4. Water adsorption versus water pressure at different temperatures on Graphon activated to 37.9% burn-off. The active surface area was covered with oxygen complex.

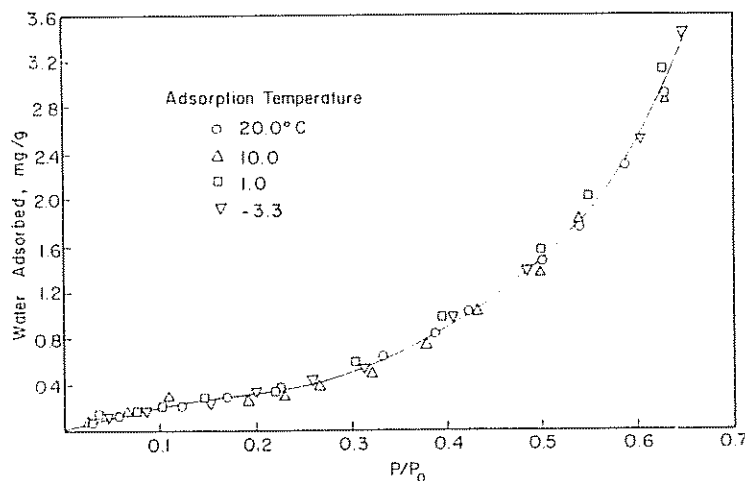


FIG. 5. Water adsorption versus water relative pressure at different temperatures on Graphon activated to 37.9% burn-off. The active surface area was covered with oxygen complex.

$$\frac{p}{W(p_0 - p)} = \frac{1}{W_m C} + \left[ \frac{C - 1}{W_m C} \right] \left[ \frac{p}{p_0} \right], \quad [1]$$

where

$W$  = weight adsorbed at pressure  $p$ ;  
 $C \simeq \exp [(E - E_L)/RT]$  according  
 to Emmett (21);

$(E - E_L)$  = difference between heat of ad-  
 sorption and heat of lique-  
 faction; and

$W_m$  = weight of adsorbate required to  
 cover a monolayer.

But it has just been shown from our ad-

sorption studies that  $(E - E_L)$  closely  $\rightarrow 0$ .  
 Thus,  $C$  closely approaches 1. In this case,  
 Eq. [1] can be simplified to give

$$\frac{p}{W(p_0 - p)} = \frac{1}{W_m}. \quad [2]$$

From Eq. [2],  $W$  equals  $W_m$  at  $p/p_0 = 0.5$ .  
 If an area of  $10.6 \text{ \AA}^2$  is assumed for the water  
 molecule adsorbed on graphitized carbon at  
 $20^\circ\text{C}$  (22, 23),  $W_m$  values can be converted  
 to surface areas. Results are summarized in  
 Table II. Agreement between the areas oc-  
 cupied by chemisorbed oxygen (ASA) and

TABLE II  
SURFACE AREAS OF ACTIVATED GRAPHON SAMPLES  
COVERED BY OXYGEN COMPLEX AND THEN  
BY WATER

Graphon burn-off (%)	Surface area (m <sup>2</sup> /gm) covered by	
	Oxygen complex	Water
9.1	1.9	2.0
24.9	3.9	4.6
37.9	4.9	5.1
70.4	5.2	5.3

those occupied by physically adsorbed water is excellent.

Of course, one is not certain that 10.6 Å<sup>2</sup> is a correct area to assign to the water molecule. This value is obtained if the usual assumption of hexagonal close packing of the adsorbate is assumed. Kiselev and co-workers (24, 25) also suggest an area of 10.6 Å<sup>2</sup> for water adsorbed on graphitized carbon. Dawson (23), basing his calculations on the fact that liquid water has a partly hydrogen-bonded structure, concludes that a more reasonable molecular area at 20°C is 10.1 Å<sup>2</sup>. If this value is taken, the water areas in Table II will be decreased by 5%; this, if anything, improves the correlation.

In any case, the authors find such close agreement between the oxygen chemisorption area and water physical adsorption area difficult to understand. Adsorption of water would be expected to be localized at lattice sites containing oxygen, as a result of hydrogen bonding. If the adsorbed water were immobile on these sites, it would be most fortuitous if the area occupied by the water molecule agreed closely with that calculated on the basis of hexagonal close packing of liquid water. Indeed, Pierce and Ewing show that even N<sub>2</sub> adsorption at 78°K on the basal plane of Graphon is to some degree localized and that the molecular area is close to 20 Å<sup>2</sup> instead of the 16.2 Å<sup>2</sup> calculated from hexagonal close packing of liquid N<sub>2</sub> (26).

It is significant that the heat of adsorption of water in the first adsorption layer was essentially equal to its heat of liquefaction. This indicates that each hydrogen in the water molecule was hydrogen bonding to a chemisorbed oxygen atom and that the

length and strength of the bonding closely approached the values found in bulk water. For this to be the case, simple calculations show that it is most likely that the two hydrogens in a water molecule were hydrogen bonding to oxygen atoms on carbon sites in adjacent basal planes of graphite. Since each chemisorbed oxygen is expected to be able to participate in the formation of two hydrogen bonds with hydrogen atoms from two different water molecules, the area occupied by a water molecule would be equal to that occupied by each carbon atom in the (10 $\bar{1}$ l) or (11 $\bar{2}$ l) plane, i.e., about 8.3 Å<sup>2</sup>. However, it is unlikely that each chemisorbed oxygen atom, in fact, was appropriately located (because of unevenness of plane termination and dangling carbon fragments) to participate in two hydrogen bonds. In this case, the average area occupied by a water molecule would be somewhat greater than 8.3 Å<sup>2</sup>.

*F. Water Adsorption on Graphon Samples Where the ASA Is Only Partially Covered with Oxygen Complex.* So far we have discussed water adsorption on Graphon samples which had their ASA completely covered with oxygen. It is also of interest to study water adsorption on Graphon where only portions of the ASA were covered by oxygen. As described previously, varying amounts of coverage were achieved by degassing a sample saturated with oxygen complex at 350°C at different temperatures up to 950°C. Figure 6 presents typical degassing results for the 24.9% burn-off Graphon sample, initially saturated with oxygen. At each temperature where there is a data point, outgassing was continued until the weight loss became immeasurable. Such times, typically, were from 1 to 2 hours. Most of the weight loss occurred between 500° and 700°C. In this run, the 250 mg sample of Graphon underwent a total weight loss of 0.14 mg or 0.056%. Thus, negligible additional gasification of carbon resulted.

Figure 7 presents water adsorption isotherms measured at 20°C on the 24.9% burn-off Graphon sample, where the ASA was covered by varying amounts of oxygen. Where the oxygen coverage is indicated as nil, the sample was heated to 950°C for 12

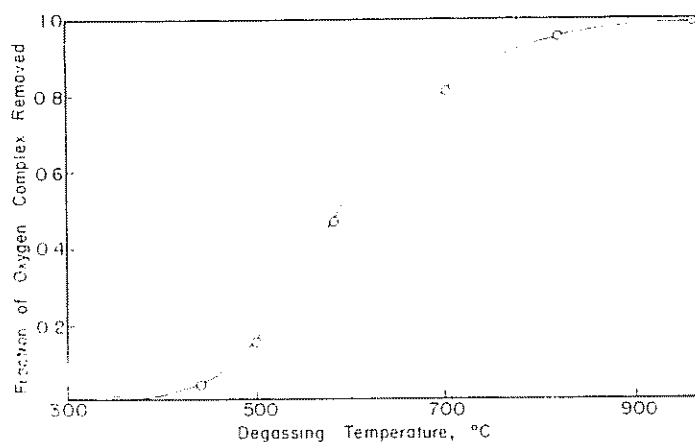


Fig. 6. Removal of oxygen complex from Graphon activated to 24.9% burn-off by high temperature degassing. Active surface was previously covered by complex at 350°C.

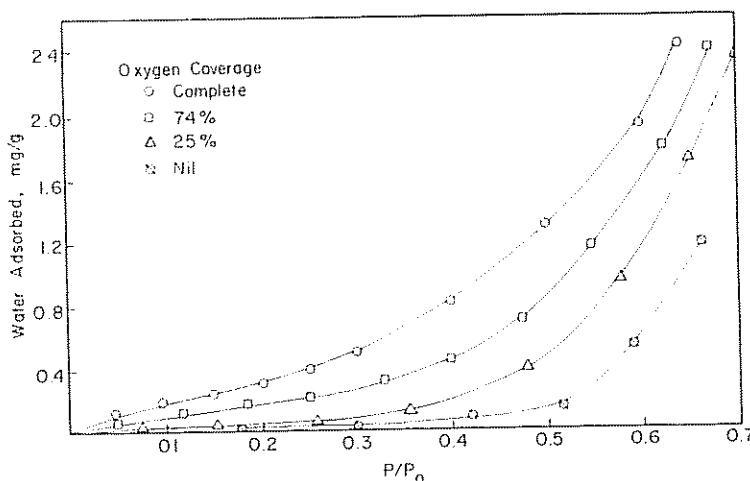


Fig. 7. Water adsorption isotherms at 20°C on Graphon activated to 24.9% burn-off, where its active surface was covered to varying extents by oxygen complex.

hours in a vacuum of  $10^{-5}$  torr. As expected, removal of oxygen complex sharply decreased water adsorption. An attempt was made to normalize the adsorption data by expressing it per unit of ASA occupied by oxygen complex, as shown in Fig. 8. Normalization of the data is reasonably good up to a relative pressure of at least 0.4 for all the samples. Clearly at 0.5 and above, however, normalization fails for the Graphon having only 25% of its ASA covered by oxygen. Water uptake was significantly greater than that predicted. Adsorption in the second layer, i.e., for  $p/p_0 > 0.5$ , would be expected to

follow a somewhat different course dependent upon the density of packing (or closeness of approach) of the water molecules in the first layer. If the first layer was densely packed with water (as was the case for complete coverage of the ASA with oxygen), subsequent adsorption would occur more or less normally with the formation of a second layer. On the other hand, if the first water layer was loosely packed (ASA coverage of 25% with oxygen, for example) adsorption at relative pressures above 0.5 would involve growth and ultimate coalescence of water clusters in the first layer (27)



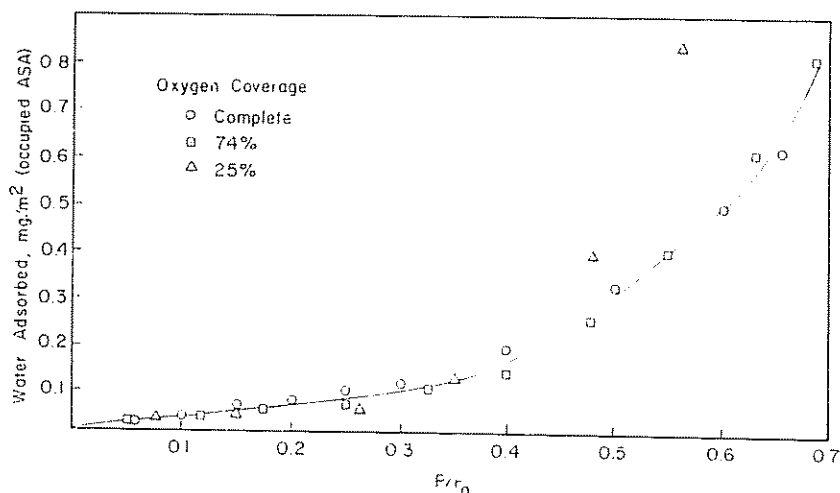


Fig. 8. Water adsorption at 20°C on Graphon activated to 24.9% burn-off. The amount adsorbed is normalized on a basis of active surface area covered by oxygen complex.

plus the formation of a second layer. The results shown in Fig. 8 are consistent with this reasoning.

Several comments can be made about the water adsorption isotherm on the Graphon sample degassed at 950°C, shown in Fig. 7. Unquestionably, in the presence of a residual pressure of  $10^{-5}$  torr, all oxygen complex was not removed from the Graphon (15). If the amount of water adsorbed at a relative pressure of 0.5 can be taken as  $W_m$  for this sample, then this value can be subtracted from  $W_m$  for the Graphon sample the ASA of which is completely covered by oxygen complex. The correction is about 10%. This result suggests that the area occupied by the water molecule in the first layer may be about 10% greater than 10.6 Å<sup>2</sup> or about 11.7 Å<sup>2</sup>.

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