

EFFECT OF OXIDATION ON THE SURFACE HETEROGENEITY OF SOME GRAPHITIZED CARBONS

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Abstract—A fraction of the surface of some graphitized carbons are energetically heterogeneous. That part of the surface which is heterogeneous has sites for which N_2 shows a higher isosteric heat of adsorption at 78°K than the uniform portion constituting the major fraction of surface and for which the heat of adsorption is constant. The effect of oxidation on this surface heterogeneity has been studied for three different graphitized carbons: Graphon, GP33, and British Pile Grade A Graphite. It was found for the Graphon and GP33 that the proportion of sites which offered high heats of adsorption to N_2 increased sharply with an increasing amount of O_2 burn-off. Although the unoxidized Pile Grade A Graphite was less homogeneous than either Graphon or GP33, burn-off did not produce such a marked increase in the fraction of heterogeneity. The effects which these changes in surface heterogeneity have on the isosteric heats of adsorption and integral molal entropy of adsorption are discussed.

1. INTRODUCTION

EARLY workers obtained linear isotherms for the adsorption of N_2 ,⁽¹⁾ O_2 ,⁽²⁾ and Ar ,⁽³⁾ on charcoal where the coverages correspond to less than 1 per cent of the monolayer capacity. Some doubt is cast on the precise linearity of these isotherms by the work of KALBERER and SCHUSTER⁽⁴⁾ who obtained a linear isotherm for the adsorption of CO_2 on silica gel despite a large variation in the calorimetric differential heat of adsorption over the same range of coverage. The inference is that either the volumetric measurements were of insufficient accuracy to disclose any departure from linearity or that some fortuitous opposing effects were operating which rendered the volume adsorbed proportional to the equilibrium pressure. The Henry's Law region of such isotherms is predicted by the statistical model proposed by WILKINS⁽⁵⁾ and by the two-dimensional model of ROWLEY and INNES.⁽⁶⁾ The linear isotherm for N_2 on a graphitized carbon black noted by ROSS and WINKLER⁽⁷⁾ was ascribed to a system in which the adsorbate behaves as an ideal two-dimensional gas on a

homogeneous surface. However, the authors did point out that the precision may have been sufficiently inadequate to conceal any departure from linearity at the lowest measured coverages. Work on the adsorption of ethyl chloride on a sample of Graphon also indicated a homogeneous type of surface,⁽⁸⁾ but at coverages less than 3 per cent the isotherms are slightly concave towards the pressure axis. This suggests that a small fraction of the surface is energetically heterogeneous. The type of heterogeneity apparent is probably the same as that observed by GRAHAM,⁽⁹⁾ who studied the adsorption of N_2 on Graphon at very low coverages. Graham concluded that this small fraction of surface which appears heterogeneous consists of irregularities in the solid surface and provides for more than one point of interaction with an adsorbate molecule.

It is quite possible that the extent of surface irregularity is dependent on the oxidation history of the sample studied. Experiments⁽¹⁰⁾ in which O_2 is admitted to a Graphon surface at 300°C indicate that only a very small fraction of the

surface is active in forming an oxygen surface complex. Furthermore, the quantity of O_2 chemisorbed is strongly dependent on the way in which the Graphon is pretreated. Thus, the amount of O_2 adsorbed is a function of the amount of burn-off to which the sample has been previously subjected.

The object of the present study was two-fold: (1) to study the low coverage adsorption of N_2 on Graphon and other graphitized carbons in order to estimate the extent of surface heterogeneity as a function of previous burn-off by O_2 , and (2), to measure the effect of changes in surface heterogeneity on the isosteric heat of adsorption and integral molal entropy of adsorption. Such a study may have two useful consequences. It may be possible to predict the extent of surface heterogeneity and perhaps the oxidation history of a carbon. Furthermore, experimental heats of adsorption should provide a reliable measure of the extent of lateral interaction, provided these forces are not masked by surface heterogeneity. An estimation of the contribution to the heat of adsorption by lateral molecular interactions would be possible once the amount of heterogeneity has been measured and allowed for.

2. EXPERIMENTAL

2.1 Materials

Graphitized Spheron-6 (Graphon) and graphitized P33 (GP33) were gifts from the Cabot Corporation. The original carbon blacks were heated to *ca.* 2750°C in an inert atmosphere. They have arithmetic mean diameters of *ca.* 200 and 1600 Å, respectively. Their surface areas (determined by the BET method using Kr as adsorbate) are 96 and 12 m²/g, respectively. The L_c dimension determined by X-ray analysis, is 50 Å for Graphon and 132 Å for GP33. The L_a dimension is approximately 78 Å for both materials. The third material used was British Pile Graphite, Grade A (BPGA), donated by the U.K.A.E.A. Its surface area, measured with Kr, is 6.3 m²/g. The L_c and L_a dimensions are 100 Å and 500 Å,⁽¹¹⁾ respectively.

To obtain samples of these three graphitic materials with different amounts of surface heterogeneity, the original materials were heated to 600°C in a silica vessel in the presence of spectroscopically pure O_2 for varying lengths of time. The amount of burn-off was estimated from the loss in weight of each sample. Each pretreated sample was

heated subsequently in the sample bulb of the adsorption apparatus to 900°C *in vacuo* for 12 hr to remove the stable carbon-oxygen complex formed during oxidation.⁽¹⁰⁾ By this means, and in addition thoroughly outgassing the glass connecting tubing, the pressure, after isolating from pumps and with cold traps in place, was 10^{-7} torr as measured with an ionization gauge. Nitrogen of greater than 99.9 per cent purity was checked by mass spectrographic analysis. No trace of any gases or vapours, including water vapour, was detectable, so the N_2 was used without any additional purification.

2.2 Apparatus

The adsorption apparatus consisted of a 1 cm dia., 5 cm long silica sample holder joined via a silica-Pyrex graded seal to a U-tube type cold trap and two mercury cut-offs isolating the dosing section and the pumps. The dosing section consisted of two accurately calibrated McLeod gauges covering a pressure range from 4.0 to 7×10^{-7} torr. These gauges also served as standard volumes from which measured doses of N_2 were admitted to the sample holder via one of the mercury cut-offs. An ionization gauge was also incorporated to ascertain the lowest pressure achieved by the high-speed mercury diffusion pump, backed by a second diffusion pump and a rotary oil pump in series. It was not possible to use the ionization gauge during an adsorption. Spurious effects were observed when this was attempted, probably because of chemisorption of N_2 by the tungsten plates of the gauge.⁽¹²⁾

All tubing connecting the sample holder with the McLeod gauges, including the U-tube cold trap, was of 1 cm uniform bore. This was a compromise between narrow tubing, which would introduce errors due to molecular diffusion, and larger bore tubing, which would increase the dead space too much. Liang's equation⁽¹³⁾ for thermomolecular flow was applied to all pressure readings taken. For volume calibrations, N_2 was expanded from either a flask of measured standard volume or one of the two McLeod gauges, into the various sections of the apparatus. Since measurements were carried out at low coverages, it was important to take into account the amount of gas adsorbed on the walls of the sample-holder and cold trap, both at 78°K during an experiment. Calibrations were

therefore carried out using N_2 over the whole range of pressure employed, with both the empty sample-holder and the U-tube cold trap at liquid N_2 temperature. By this means the apparent volume of the adsorption section was calculated as a function of the equilibrium pressure of N_2 .

3. RESULTS

Extensive preliminary experiments indicated that there was a marked increase in the adsorptive properties of Graphon in the low coverage range after a sample had been subjected to varying amounts of burn-off with O_2 at $600^\circ C$. Furthermore, the specific surface area of the material increased as a function of burn-off. Accordingly, detailed adsorption experiments, with much attention to the precision of pressure measurements, were carried out on samples of Graphon which had been burned in O_2 for various times to

produce the desired extents of burn-off. Similar burn-off experiments using GP33 and BPGA also gave a material of greater surface activity and increased specific surface area. Detailed adsorption experiments at low coverages for the latter graphitized carbons were therefore compared with the results obtained for Graphon. The range of coverage studied in detail was from 0.2 to 10 per cent, extending over a pressure range of 1×10^{-5} torr (relative pressure 2×10^{-8}) to 1×10^{-2} torr (relative pressure 2×10^{-5}). Experiments were conducted on such samples by allowing N_2 to adsorb accumulatively in successive doses; this proved to be as reliable as GRAHAM's procedure⁽⁹⁾ of adsorbing and desorbing a single dose before admitting a second and larger dose, the surface having been previously conditioned by many such cycles before recording equilibrium pressures. Small successive increments in the amount of

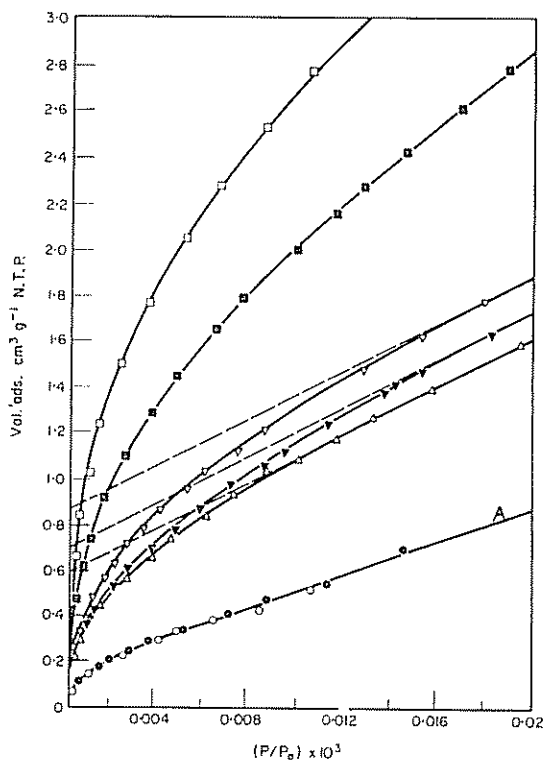


FIG. 1(a). N_2 isotherms at $77.8^\circ K$ on Graphon. Symbols for percentage burn-off: \square , 37%; \blacksquare , 24%; ∇ , 6.5%; \blacktriangledown , 4.5%; \triangle , 1.6%; \circ and \odot , unoxidized.

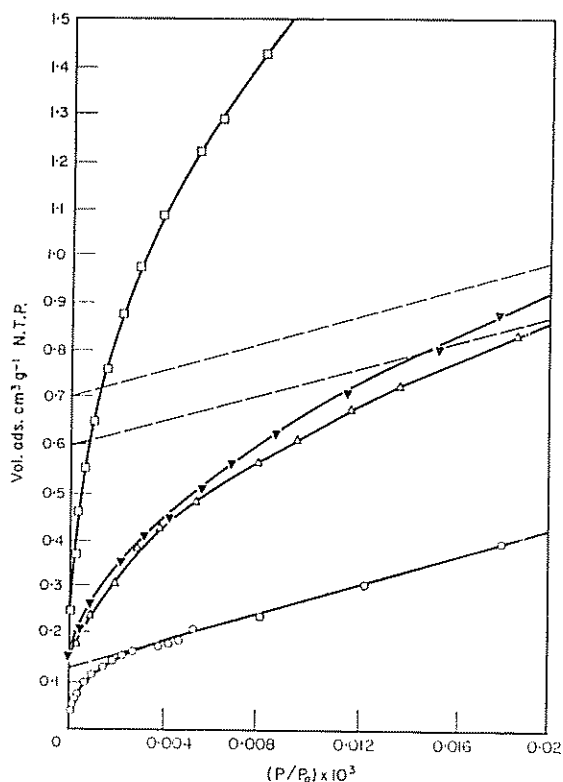


FIG. 1(b). N_2 isotherms at $90.4^\circ K$ on Graphon. Symbols for percentage burn-off: \square , 37%; ∇ , 4.5%; \triangle , 1.6%; \circ , unoxidized.

adsorbed gas were considered a desirable feature when applying thermodynamic equations to the calculation of isosteric heats of adsorption from experimental isotherms. Since the reproducibility of the experimental results was good as evidenced by repeat runs, cumulative errors were regarded as negligible.

Adsorption isotherms were determined at two temperatures, viz. 77.8 and 90.4°K using fresh liquid N₂ and liquid O₂ as refrigerants. The temperature of the cold bath was checked occasionally with a gas thermometer. The temperature of either refrigerant did not fluctuate by more than $\pm 0.3^\circ\text{K}$ during the entire course of a run, although a continuous supply of fresh refrigerant was necessary. Figures 1(a) and (b) shows a series of adsorption isotherms for N₂ on Graphon burned-off by various amounts up to 37 per cent. At both 77.8 and 90.4°K all the isotherms show an initial curvature, concave to the relative pressure axis and then an extended linear portion. The original sample of Graphon, not reacted with O₂, but thoroughly outgassed to 900°C as for all other samples, gave a linear isotherm, represented by A, down to a relative pressure of 3×10^{-6} , when it curved sharply downward towards the relative pressure axis. As may be seen by inspecting

curve A, reproducibility was extremely good. Thus the whole curve could be reproduced by two separate experiments (indicated by different symbols) on the same sample at different times. Although a detailed study was only made over the relative pressure range 2×10^{-8} – 2×10^{-5} , each of the isotherms was continued to higher relative pressures of 5×10^{-3} , corresponding to the completion of a monolayer. Only in this way was it possible to extrapolate the linear portion of the isotherms with any confidence so that an estimate could be made of the fraction of surface which was heterogeneous. Each isotherm was plotted on large graph paper to ameliorate such extrapolation. It is not possible to show such extended plots in a single diagram, and for reasons of conciseness the higher pressure isotherms have not been included in this paper.

As the amount of burn-off is increased, the curved part of the isotherm becomes steeper and continues to higher relative pressures. Following GRAHAM,⁽⁹⁾ the intercept on the ordinate of the extrapolated linear portion was assumed to represent the total amount of N₂ adsorbed by those sites offering a higher heat of adsorption than the greater majority of sites contained by the energetically homogeneous portion of surface. Thus the

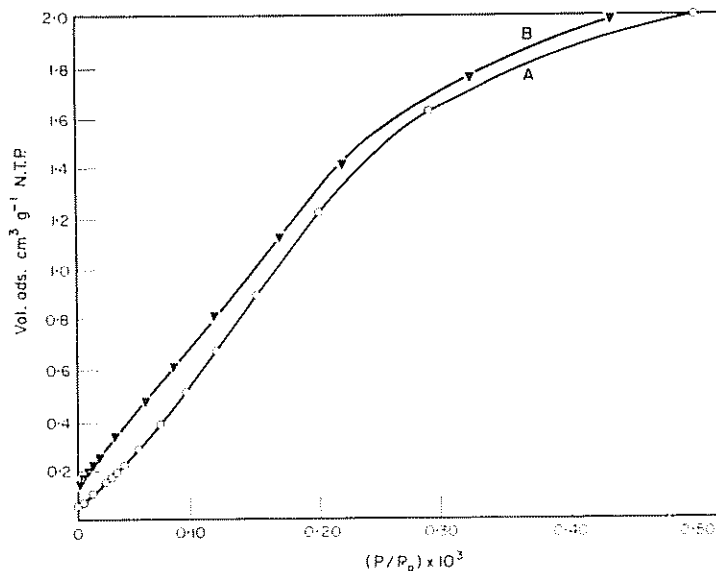


FIG. 2. N₂ isotherms at 77.8°K on GP33 extended to higher relative pressures. Symbols for percentage burn-off: ▼, 5.1%; O, unoxidized.

fraction of surface which is heterogeneous can be represented by the ratio V_i/V_m , where V_i is the intercept on the ordinate and V_m is the monolayer volume. Curve A, Fig. 4 shows how the fraction of heterogeneous surface varies as a function of burn-off for Graphon. It is quite evident that the extent of heterogeneity increases sharply as a function of previous burn-off.

Isotherms were also obtained at 77.8 and 90.4°K for GP33 over a wide range of burn-off. Again, the intercept of the extrapolated linear region of the isotherms was used to estimate fractional heterogeneity. Curve B, Fig. 4 shows that the fraction of heterogeneity also increases sharply with burn-off for GP33. When compared with Graphon, however, it is obvious that GP33 has a more homogeneous surface at any given level of burn-off.

It is seen from Fig. 2 that the isotherm for unoxidized GP33 is not linear but displays a slightly convex curvature towards the relative pressure axis over the relative pressure range from $ca. 2 \times 10^{-5}$ to 1.5×10^{-4} . This is in contrast to the linear isotherm for Graphon over the same relative pressure range. There is no reason to doubt the reality of this slight curvature as it is greater than could be accounted for by experimental error and, moreover, is reproducible. GRAHAM⁽⁹⁾ noted the

same behaviour for GP33 and, from an analysis of isosteric heats of adsorption in this region of coverage, concluded that the contribution of an attractive interaction between adsorbed molecules to the total heat of adsorption increases more rapidly for GP33 than for Graphon. The isotherm B in Fig. 2 shows that after only 5 per cent burn-off of GP33 the convex nature of the isotherm is removed.

Experiments with BPGA were not quite as reproducible as those with Graphon or GP33. For a given oxidized sample of BPGA, isotherms were readily reproducible (see isotherm A, Fig. 3), so there is no question of any spurious results for a particular sample due to any lack of equilibration. However, two different samples oxidized by roughly the same amount, *ca.* 2.8 and 2.5 per cent, gave isotherms (A and B, Fig. 3) differing by $0.006 \text{ cm}^3/\text{g}$ (expressed at NTP) for any given relative pressure in the linear range. This did not occur for either Graphon or GP33. The difference between A and B may be taken to represent the order of reproducibility obtainable with BPGA. This is possibly caused by BPGA not oxidizing uniformly from sample to sample, resulting in a slight difference in the fraction of heterogeneous sites. On the other hand, the fact that the fraction

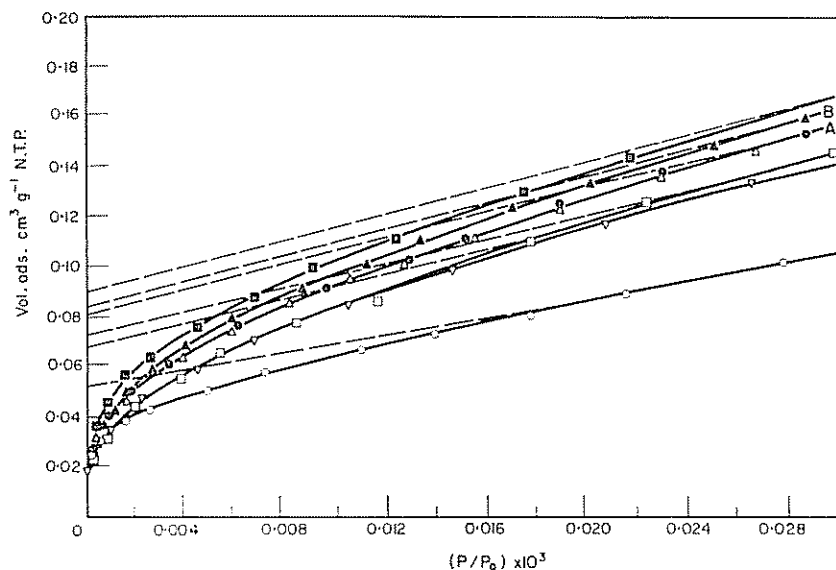


FIG. 3. N_2 isotherms at 77.8°K on BPGA. Symbols for percentage burn-off: ∇ , 17%; \square , 13%; \blacksquare , 4.3%; \triangle and \odot , 2.9%; \blacktriangle , 2.5%.

of heterogeneity is a maximum at around 4 per cent burn-off cannot be explained by irreproducible oxidation.

4. DISCUSSION

Inspection of Fig. 4 shows that unoxidized BPGA is more heterogeneous than Graphon which, in turn, is more heterogeneous than GP33. Although the unoxidized BPGA was the most heterogeneous of the original materials studied, Fig. 4 shows that burn-off did not produce such a marked increase in its fraction of heterogeneity as for the other materials. Furthermore, BPGA is the only material which first shows an increasing proportion of heterogeneous sites and subsequently, after about 4 per cent burn-off, a decreasing proportion of heterogeneous sites, the fraction almost decreasing to the value for the

unoxidized material. It may be inferred that there is something peculiar to the structure of BPGA which is not shared by either Graphon or GP33.

Table 1 shows how the surface area (measured *in situ* using Kr at 77.8°K) of each material is affected by burn-off. It is seen that the surface area of BPGA goes through a maximum and that this maximum corresponds closely to the maximum of the curve in Fig. 4 showing the variation in surface heterogeneity as a function of burn-off. Such an effect of burn-off on the surface area of a material similar to BPGA has been noted before.⁽¹⁴⁾ It may be supposed that the surface area of a material will go through a maximum, when oxidized, if the pore structure consists of a large number of very fine pores. Initially, the pores will increase in diameter and thus increase the internal

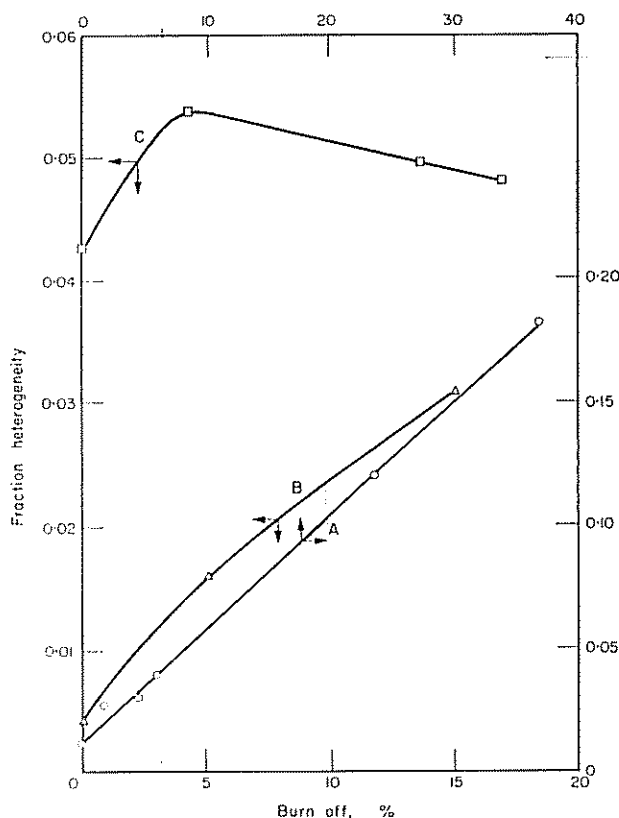


FIG. 4. Fraction of surface heterogeneity as a function of burn-off, as calculated from the 77.8°K isotherms.
Symbols: ○, Graphon; △, GP33; □, BPGA.

TABLE I. SURFACE AREAS AS A FUNCTION OF BURN-OFF

% Burn-off	Graphon				GP33			BPGA			
	0.0	1.6	4.5	37	0.0	5.1	15.2	0.0	4.3	13.7	17.0
Surface area (m ² /g)	96.1	117.8	121.7	134.5	12.2	16.2	18.9	6.3	8.5	7.2	7.0

surface area, and hence, the total surface area. If the small diameter pores are sufficiently close originally, sooner or later after enlargement by oxidation the pores will merge into one another giving rise to a completely different pore structure: the whole material would now gradually erode with a concomitant decrease in surface area. This need not conflict with the experimental fact that BPGA is a relatively non-porous material because prior to oxidation, all the assumed narrow pores may be closed by a thin surface skin. An alternative explanation is that some pores are too narrow for penetration until they have been sufficiently enlarged by O₂. That Graphon or GP33 do not behave like BPGA suggests, therefore, that their geometric structures are different. A pore size determination of Graphon* indicated that the unoxidized material does contain a small number of fairly large diameter pores. In this case oxidation

increases the diameter and length of these pores, hence increasing the surface area as before. However, if the pores are not in close proximity to one another and their distribution is such that they do not merge, the surface area will continue to increase up to quite high burn-offs. It is possible that a similar argument may apply to GP33. Comparison of Fig. 4 with Table 1 shows that the general trend of results for the fraction of heterogeneity and surface areas, both as a function of burn-off, are very similar. This really implies that the energetically heterogeneous sites are fairly evenly distributed throughout each of the materials studied.

The isosteric heats of adsorption q_{ist} , for Graphon and GP33 were deduced from each of the pairs of adsorption isotherms studied at 77.8 and 90.4°K. Figure 5 shows the results obtained for Graphon. Very similar results were obtained for GP33. It is quite evident, both for Graphon and for GP33, that an increase in burn-off in-

*Kindly measured for us by AERE, Harwell, U.K.

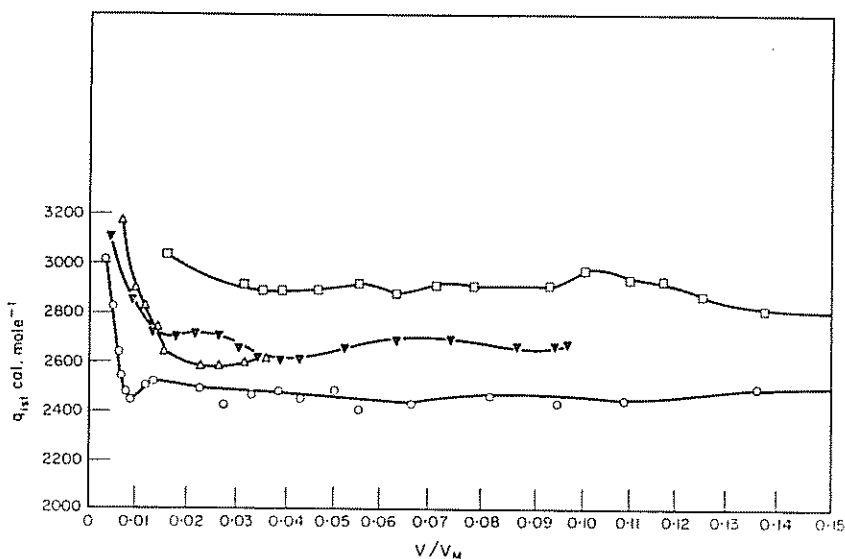


FIG. 5. Isosteric heats of adsorption for N₂ on Graphon. Symbols for percentage burn-off: □, 37%; ▽, 4.5%; △, 1.6%; ○, unoxidized.

increases the isosteric heats of adsorption at low coverages. At higher coverages the curves begin to converge. For example, the heat of adsorption for the 37 per cent burn-off sample approaches to within 3 per cent of the original Graphon at a coverage of 0.27. The curve obtained for unoxidized Graphon follows a similar trend to that obtained by BARRER⁽¹⁵⁾ who studied the adsorption of N_2 , amongst other gases, on an outgassed graphite. BARRER noted that the isosteric heat of adsorption at low coverage was twice the value found at higher coverages and ascribed this to the possibility of a N_2 molecule adsorbing at intersections of planes and boundaries. While the value of 2.40 ± 0.10 kcal/mole obtained by us for the homogeneous portion of the isotherms corresponds closely to the value found by BARRER at coverages of about 10 per cent, the highest value we could confidently calculate from the isotherm was 3.03 ± 0.10 kcal/mole at a coverage of 1.55 per cent, obtained for Graphon burned-off to 37 per cent. Less precise values at very much lower coverages were calculated from points observed experimentally but not shown in the isotherms. The precision of measurement is very much reduced at very low pressures and also the values of q_{ist} are very sensitive to pressure because of the logarithmic form of the integrated Clausius-Clapeyron equation. However, we are able to quote values of 4.2 ± 0.2 kcal/mole for coverages not more than 0.3 per cent. Hence BARRER's earlier observations are confirmed. The obvious increase in q_{ist} at a given coverage with increase in burn-off is most simply explained in terms of a large fraction of heterogeneous sites available for adsorption.

It is of some interest and relevance to examine curves obtained for the integral molal entropy of adsorption as a function of coverage and burn-off. HILL's method⁽¹⁶⁾ of assessing experimental values of the integral molal entropy S_s of the adsorbed state with reference to the entropy S_L^0 of the liquid at its saturated vapour pressure was adopted. Experimental values for $(S_s - S_L^0)$ were thus obtained as a function of coverage for both Graphon and GP33 for various burn-offs. Figure 6 clearly shows that for Graphon the integral molal entropy increases with burn-off. Similar results were found for GP33. Hence to conclude that higher heats of adsorption at the lowest measured relative pressures are indicative of stronger binding may be quite

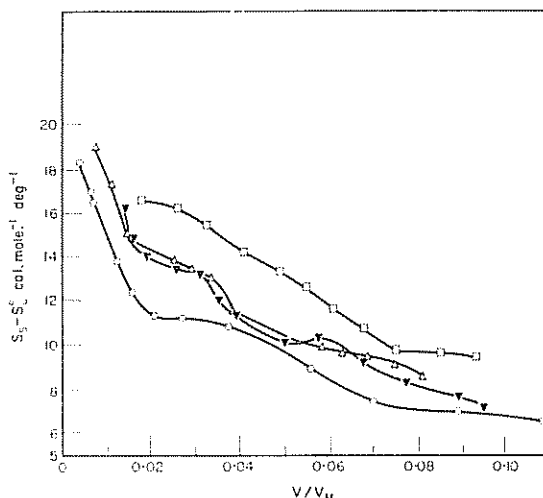


FIG. 6. Integral molal entropies for N_2 on Graphon. Symbols for percentage burn-off: □, 37%; ▽, 4.5%; △, 1.6%; ○, unoxidized.

misleading. In the light of JOYNER and EMMETT's work⁽¹⁷⁾ where the differential entropy of the adsorbed nitrogen phase on Graphon is positive with respect to that on Spheron, such a result is surprising. However, as pointed out by HILL⁽¹⁶⁾ it is often misleading to compare differential entropies with integral molal entropies and the latter quantity is of more direct value in interpreting the mode in which the adsorbed phase exists. It was suggested by BEEBE and co-workers⁽¹⁸⁾ that the highly active centres on Spheron produce a very ordered adsorbed phase and are eliminated when graphitized, giving rise to a more homogeneous surface with a less ordered adsorbed phase. Therefore, it appears that oxidation, having increased the fraction of active centres responsible for strong nitrogen adsorption, produces an adsorbed phase with an entropy even more positive than that associated with either Graphon or Spheron. This behaviour can be understood if the observed increase in $(S_s - S_L^0)$ with increased heterogeneity is due to decreased mobility as more and more new edges or lattice intersections are exposed. Thus, adsorbed molecules are localized and this results in an increase in the configurational entropy⁽¹⁹⁾ with increasing burn-off for fixed values of coverage.

It is of interest to investigate whether, in fact, the configurational entropy is playing a significant

TABLE 2. COMPARISON OF EXPERIMENTAL AND CALCULATED ENTROPIES

	Graphon						GP33					
	Unoxidized			37% burn-off			Unoxidized			15% burn-off		
Coverage	0.005	0.015	0.100	0.005	0.015	0.100	0.005	0.015	0.100	0.005	0.015	0.100
$(S_G - S_s)$, cal/mole/ degree	29.8	29.4	29.5	*36.6	32.7	31.7	29.4	29.2	28.1	35.1	32.3	30.8
$(S_{tr})_3 - (S_{tr})_2 - S_{config}$	26.5	26.2	27.9	*34.9	33.4	32.4	24.2	24.7	27.6	30.2	29.3	30.0

*Extrapolated values

role in affecting $(S_s - S_s^0)$. By subtracting this term from $(S_G - S_L^0)$, where S_G is the entropy of gaseous N_2 at a pressure of p atm and $77.8^\circ K$, one obtains the value $(S_G - S_s)$, which is the entropy loss on adsorption from the gas phase. Values of S_G and S_L^0 are available⁽²⁰⁾ and are derived by application of the Third Law of Thermodynamics to experimentally measured specific heats. This experimental entropy loss $(S_G - S_s)$ may now be compared with a theoretical entropy loss. The entropy of the gas will consist of contributions from three translational degrees of freedom, two rotational degrees of freedom and one vibrational degree of freedom. Upon adsorption at least one degree of translational freedom is lost. The vibrational degree of freedom should be relatively unaffected by physical adsorption; in any case, the vibrational contribution to the entropy of nitrogen at $77.8^\circ K$ is negligible. Based on the reasoning of GRAHAM⁽²¹⁾ for adsorption of water on Graphon, the change in the rotational contribution to the entropy upon adsorption of nitrogen is taken as small and is neglected in this approximation. Upon adsorption, the adsorbed species may gain configurational entropy; this entropy can be significant at low coverages. Hence one can write $(S_G - S_s) \approx (S_{tr})_3 - (S_{tr})_2 - S_{config}$.

Taking accepted equations for the translational and configurational entropy terms,^(19, 22) the calculated and experimental entropies are in relatively good agreement as is seen in Table 2. It is concluded that at low coverages the configurational entropy is significant. Therefore, there is a considerable loss in mobility of adsorbed N_2 on Graphon and GP33 at $77.8^\circ K$.

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REFERENCES

1. CHAPLIN R., *Phil. Mag.* **2**, 1198 (1926).
2. MAGNUS A. and GRAHLING K., *Z. Phys. Chem.* **A145**, 27 (1929).
3. MAGNUS A. and KALBERER W., *Z. Anorg. Chem.* **164**, 357 (1927).
4. KALBERER W. and SCHUSTER C., *Z. Phys. Chem.* **A141**, 270 (1939).
5. WILKINS F. J., *Proc. Roy. Soc., Lond.* **A164**, 496 (1938).
6. ROWLEY H. H. and INNES W. B., *J. Phys. Chem.* **45**, 158 (1941).
7. ROSS S. and WINKLER W., *J. Colloid Sci.* **10**, 319 (1955).
8. PIERCE C. and SMITH R. N., *J. Am. Chem. Soc.* **75**, 846 (1953).
9. GRAHAM D., *J. Phys. Chem.* **61**, 49 (1957).
10. LAINE N. R., VASTOLA F. J. and WALKER P. L. JR., *Proceedings of the Fifth Carbon Conference*, p. 211. Pergamon Press, Oxford (1963).
11. WILSON S., Private communication A.E.R.E., Harwell.
12. TRAPNELL B. M. W., *Proc. Roy. Soc., Lond.* **A218**, 566 (1953).
13. LIANG S. C., *J. Phys. Chem.* **57**, 910 (1953).
14. WALKER P. L. JR. and RAATS E., *J. Phys. Chem.* **60**, 364 (1956).
15. BARRER R. M., *Proc. Roy. Soc., Lond.* **A161**, 476 (1937).
16. HILL T. L., *J. Chem. Phys.* **17**, 520 (1949).
17. JOYNER L. G. and EMMETT P. H., *J. Am. Chem. Soc.* **73**, 5102 (1951).
18. BEEBE R. A., BISCOE J., SMITH W. R. and WENDELL C. B., *J. Am. Chem. Soc.* **69**, 95 (1947).
19. KEMBALL C., *Advances in Catalysis*, Vol. 2, p. 233. Academic Press, New York (1950).
20. LANDOLT-BORNSTEIN, *Values of Functions*, 6th Ed., Vol. 2, p. 405.
21. GRAHAM D., *J. Phys. Chem.* **60**, 1022 (1956).
22. GLASSTONE S., *Thermodynamics for Chemists*, p. 190. Van Nostrand, New York (1947).

