

## Effect of Surface Heterogeneity of Carbon on the Two-Dimensional Critical Temperature of Adsorbed Xenon

O. P. MAHAJAN AND P. L. WALKER, JR.

*Department of Materials Science, Pennsylvania State University, University Park, Pennsylvania*

Received February 5, 1969; revised March 12, 1969

Adsorption of Xe on three graphitized carbon blacks of different particle and crystallite size has been measured at 195°K, both before and after oxidation of the blacks to different levels of gasification. Gasification is known to increase the surface heterogeneity of the blacks. Using an approach proposed by Hill for mobile layers with adsorbate interaction on a surface, two dimensional critical temperatures,  $T_{2c}$ , for Xe have been estimated. The  $T_{2c}$  decreases significantly and continuously as the extent of surface heterogeneity is increased. It is suggested that this decrease is attributable to an increase in the magnitude of the potential barrier for the translation of Xe across the surface, as recently proposed by Steele and Karl.

### I. INTRODUCTION

It is well known (1-3) that at not too low temperatures many gases adsorbed on charcoal, graphitized carbon blacks, graphite, and alkali halides behave as two-dimensional mobile films with adsorbate-adsorbate interactions. The existence of first order phase changes, corresponding to two-dimensional condensation, has been confirmed in several cases. It has invariably been found that two-dimensional condensation occurs at temperatures considerably below the three-dimensional critical temperature of the bulk gas (1, 2). Hill (4) and deBoer (1) have predicted that for spherical isotropic molecules, the ratio of the two-dimensional critical temperature ( $T_{2c}$ ) to the three-dimensional critical temperature of the bulk gas ( $T_{3c}$ ) should be 0.5. Devonshire (5), using the Lennard-Jones and Devonshire (6) theory of liquids, has suggested this ratio to be 0.53. However, numerous studies even on relatively homogeneous surfaces show conclusively that the experimental ratio is significantly lower than the theoretical value (1, 2). While some work has been reported (7-10) in the case of relatively homogeneous graphitized carbon blacks, the effect of their surface heterogeneity, which can be introduced and modi-

fied by carbon gasification (11, 12), on the two-dimensional critical temperature has not been investigated. The present communication describes one such attempt.

### II. EXPERIMENTAL

*A. Materials.* Highly graphitized carbon blacks Sterling MT, Sterling FT and Graphon were used as adsorbents. These samples, obtained from the Cabot Corporation, were heated above 2700°C. Their arithmetic mean diameter from electron microscopy are 3000, 1940, and 235Å. Their Xe BET surface areas are 6.7, 11.0, and 90 m<sup>2</sup>/gm.

Research grade Xe from the Matheson Company was used as the adsorbate. The impurity content, as specified by the manufacturer, was: N<sub>2</sub>, 3ppm and Kr, 15ppm. Before each adsorption run, the gas was purified by cryogenic pumping. Its saturation vapor pressure at the adsorption temperature, 195°K, was taken as 3200 Torr.

*B. Activation.* Sterling FT and Graphon were oxidized to different levels of burn-off, up to 37.9%, in a stream of dry air at 500°C to increase the extent of surface heterogeneity (11, 12). Details of the process have been described elsewhere (13). It has been shown that oxygen attacks the edges of the graphite

crystallites, i.e. on carbon atoms located on (101) and (112) planes (14). Following oxidation, the samples were heated to 950°C and held for 1 hour in a flowing high-purity N<sub>2</sub> stream to desorb most of the oxygen complexes.

Activation produces a minor increase in total surface area but a major increase in active area (11), which is responsible for the surface heterogeneity. For instance, in the case of Graphon after 37.9% burn-off, the total area increases only about 1.5-fold whereas the active area increases about 25-fold. However, even at this level of burn-off, the active area is less than 4% of the total surface area (13).

*C. Sorption Studies.* Sorption was followed gravimetrically using a Cahn RG Electrobalance. A sample weight of ca 0.4 gm was taken in a thin-walled quartz bucket. Quartz wool was packed on top of the sample. The bucket was suspended from the balance arm by a platinum wire. Before the adsorption run, the sample was outgassed at 600°C to <10<sup>-6</sup> Torr using a Vacion pump. Walker and Janov (13) have reported recently that most of the oxygen chemisorbed on Graphon at 350°C can be eliminated between 600–700°C. In the present studies, a higher temperature of outgassing was not used in order to circumvent the possibility of interactions between silicon and carbon at elevated temperatures.

After outgassing, the sample was cooled to room temperature *in vacuo*. It was then surrounded by a bath of dry ice and acetone and allowed to come to thermal equilibrium. Weight changes were recorded on a 1 mV Nesco Recorder. The extent of adsorption for each point of the isotherm was measured after 30 min; equilibrium was attained well within this period.

### III. THEORY

Walker *et al.* (15) have reported recently that Xe adsorbed on Graphon and Sterling MT at 195°K obeys Henry's law at low surface coverages (10<sup>-10</sup>–10<sup>-6</sup>); at higher coverages the adsorbed phase behaves as a two-dimensional mobile layer with adsorbate-adsorbate interactions. Hill (4, 16) has proposed the following equation for mobile monolayers with interaction for a homoge-

neous surface:

$$p = \frac{(2\pi m)^{1/2}(kT)^{3/2}}{h\beta} \frac{1}{j_n} \exp(-\epsilon_1/kT) \cdot \frac{\theta}{1-\theta} \exp\left(\frac{\theta}{1-\theta} - \frac{2\alpha\theta}{\beta kT}\right) \quad (1)$$

where  $j_n$  is the partition function for vibrations of the adsorbed molecules normal to the surface,  $\epsilon_1$  is the energy of adsorption at 0°K,  $\theta$  is the surface coverage,  $\alpha$  is the value of the energy of adsorbate-adsorbate interaction, and  $\beta$  is the area occupied by an adsorbed molecule in a complete monolayer. The constants  $\alpha$  and  $\beta$  are thus the two-dimensional analogs of the three-dimensional van der Waals constants. Equation (1) can be written as

$$p = \kappa \frac{\theta}{1-\theta} \exp\left(\frac{\theta}{1-\theta} - \frac{2\alpha\theta}{\beta kT}\right) \quad (2)$$

where

$$\kappa = \frac{(2\pi m)^{1/2}(kT)^{3/2}}{h\beta} \frac{1}{j_n} \exp(-\epsilon_1/kT)$$

On rearrangement, Eq. (2) can be written as

$$W = \ln \frac{\theta}{1-\theta} - \ln p + \frac{\theta}{1-\theta} = -\ln \kappa + \frac{2\alpha\theta}{\beta kT} \quad (3)$$

so that from the plot of  $W$  versus  $\theta$ , the value of  $2\alpha/\beta kT$  can be obtained from the slope of the straight line. Further, it has been shown that  $T_{c2} = 8\alpha/27\beta k$ , if the van der Waals Equation for the adsorbed layer is obeyed (4). Therefore, Eq. (3), in conjunction with the above equation, can be used to determine the apparent two-dimensional critical temperature.

### IV. RESULTS AND DISCUSSION

Representative plots, according to Eq. (3), on original samples of Sterling FT and Graphon are shown in Fig. 1. The data for Sterling MT superimposes exactly on the Sterling FT curve. It is seen that the straight line relationship, as demanded by Eq. (3), is obtained only for a limited range of surface coverage. When the data are plotted on an extended scale, a reasonably good straight

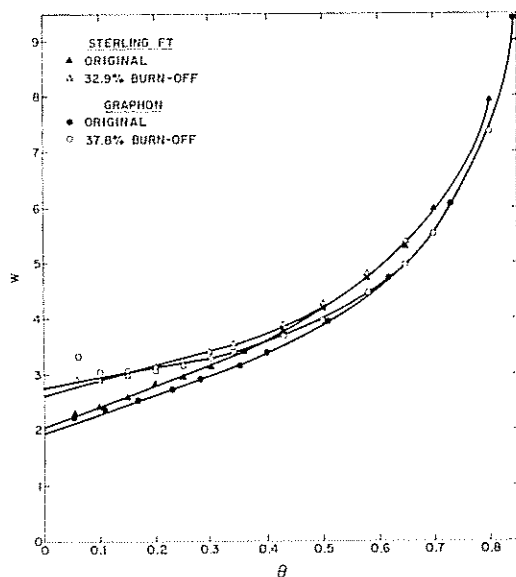


FIG. 1. Plots of equation (3) for original Sterling FT and Graphon and samples following maximum extent of gasification. Xenon adsorption at 195°K.

line relationship is obtained over the surface coverage range 0.10–0.35. Ross and Winkler (7, 8) have reported that Kr, Ar, and N<sub>2</sub> isotherms on graphitized carbon black P-33 (2700°C), which is the same as Sterling FT, obey Eq. (3) over the surface coverage region 0.10–0.50.

Plots on Graphon and Sterling FT subjected to 38 and 33% burn-off, respectively, are also included in Fig. 1. For a given black, gasification produces a marked change in the shape of the curve at surface coverages less than 0.40. In the case of 16, 25, and 38% burn-off Graphon samples, Eq. (3) is obeyed in the surface coverage region 0.15–0.35. For all the samples studied, slopes of the linear regions of the plots were calculated by the least square method.

Values of  $\alpha/\beta$ ,  $T_{2C}$ , and the ratio  $T_{2C}/T_{3C}$  for different samples are given in Table I. The ratios for the original Sterling FT, Sterling MT and Graphon are 0.400, 0.397, and 0.376, respectively. These values are quite close to those reported for other gases adsorbed on relatively homogeneous surfaces of graphitized carbon blacks (7–10). Ross and Winkler (8), who followed a similar approach

TABLE I  
MONOLAYER CAPACITIES AND PARAMETERS DESCRIBING XENON ADSORPTION ON GRAPHITIZED CARBON BLACKS OF VARYING SURFACE HETEROGENEITY

Sample	Monolayer capacity (ml/gm)	$\alpha/\beta$ (joules/mole $\times 10^{-3}$ )	$T_{2C}$ , K	$T_{2C}/T_{3C}$
Sterling MT	1.02	3.24	115.5	0.399
Sterling FT				
Original	1.67	3.19	116.0	0.400
9.6% burn-off	1.78	2.56	91.4	0.315
32.9% burn-off	1.87	2.27	80.9	0.279
Graphon				
Original	13.7	3.06	109.0	0.376
3.6% burn-off	14.4	2.32	83.0	0.287
15.8% burn-off	17.1	2.06	73.7	0.254
24.8% burn-off	18.1	1.79	63.8	0.220
37.8% burn-off	19.9	1.53	54.6	0.188

to ours, have shown that the experimental value of  $T_{2C}$  has a real physical significance, because two-dimensional condensation was observed by them below the  $T_{2C}$  value. Recently, Steele and Karl (17) measured the heat capacities of Graphon both in the absence of adsorbate and in the presence of about one half a monolayer of Ne, Ar, and Kr. They ascribed the maxima in the heat capacity curve, when the adsorbate was present, to the two-dimensional critical point. The ratios of  $T_{2C}/T_{3C}$  reported by them for Ne, Ar, and Kr were 0.36, 0.44, and 0.41. The authors note that a value of 0.40 for the ratio of  $T_{2C}/T_{3C}$  for Xe on Sterling MT, as reported by us, appears to be quite reasonable on the basis of their results. Thus, these two different independent approaches, which give similar results, lend support to the use of Eq. (3) to estimate  $T_{2C}$ .

It is interesting to note that the experimental ratio of  $T_{2C}/T_{3C}$  for the three graphitized carbon blacks is significantly less than the theoretical value of 0.5 predicted by Hill (4) and deBoer (1). Equation (3) has been explicitly derived for a homogeneous surface (4, 16). However, an ideal homogeneous surface is far from a reality. In addition to traces of impurities, some heterogeneity is introduced by point and line defects in the basal

plane of the crystallites and by crystallite boundaries. It is known that a fraction of the surface of graphitized carbons is energetically heterogeneous (12).

The value of  $T_{2c}$  for Graphon is lower than that for Sterling MT and Sterling FT. The particle size of Graphon is significantly less than that of the other samples. Since upon graphitization the growth in crystallite size is limited by the particle size, Graphon also has a significantly smaller crystallite size than the Sterling samples. Hence, it would also possess a greater density of crystallite boundaries, along which are located high energy sites. Others also conclude that Graphon is more heterogeneous than the lower area Sterling FT and Sterling MT (15, 18, 19). Thus, it appears that the departure of the experimental value of  $T_{2c}$  from the theoretical value can be used as a criterion of surface heterogeneity of the carbon. This suggestion receives support when the results for samples of different levels of burn-off are considered (Table I). It is seen that for a given black as the extent of surface heterogeneity is increased, as a result of progressive activation, the value of  $T_{2c}$  decreases. For instance, in the case of Graphon, the value decreases from 109°K for the original sample to 54.6°K for the 38% burn-off sample. The effect is not so marked in the case of Sterling FT where the value drops from 116°K for the original sample to 80.9°K for the 33% burn-off sample, thus suggesting that under comparable levels of burn-off, Graphon is more heterogeneous than Sterling FT. The effect of gasification on changing the  $V_m$  value (that is, monolayer capacity) of the two blacks is also different. In the case of Graphon,  $V_m$  increases from 13.7 ml/gm for the original sample to 19.9 ml/gm for the 38% burn-off sample; whereas for Sterling FT the value increases from 1.67 ml/gm for the original sample to 1.88 ml/gm for the 33% burn-off sample.

For gases adsorbed on ionic substrates, deBoer (1) has attributed the fact that the two-dimensional critical temperature is lower than the theoretical value to the mutual repulsion of dipoles induced in the adsorbed molecules by the ionic lattice of the adsorbents. This leads to decreased adsorbate-

adsorbate interactions, that is the value of  $\alpha$  in Eq. (3) decreases. He has also reported (20) that the values of  $\alpha$  for gases adsorbed on charcoal are always far lower than the theoretical ones and very often negative. Since the polarization of adsorbed molecules by the field of charcoal has been reported by Magnus (21, 22), deBoer has suggested that the dipoles induced in the adsorbed molecules tend to repel each other thus lowering the value of  $T_{2c}$ . However, the magnitude of these induced dipoles has been reported to be too high in comparison to the estimates from contact potentials (23) and work function lowering (24). It has been suggested (25) that a part of the repulsion must be due to a mechanism other than the ordinary electrostatic polarization. Based on a third-order perturbation treatment, Sinanoglu and Pitzer (25) have postulated the existence of three-body repulsive forces for spherical molecules in the presence of a semi-infinite surface. The existence of such forces has also been advocated by McLachlan (26). It has been argued (25) that the three-body forces should become appreciable when the third-body is a large surface. In addition to the induced dipoles caused by the classical electrostatic effect, the three-body repulsive forces can also cause a lowering of  $T_{2c}$ . deBoer and Kruyer (27) have reported the same value of the induced dipole moment for a gas adsorbed on various kinds of charcoal and graphite. The turbostratic charcoals are definitely more heterogeneous than graphite, which is composed of larger and more aligned crystallites. If surface heterogeneity has no effect on the magnitude of the induced dipole moment, as reported by deBoer and Kruyer, the polarization effect alone cannot explain the variation of two-dimensional critical temperature with surface heterogeneity. More recently, deBoer and Broekhoff (28) have reported that no polarization of Kr atoms takes place upon adsorption on Sterling FT. Ross and Olivier (2) suggest that differences in  $W$  vs.  $\theta$  plots and two-dimensional critical temperatures less than the theoretical value can be explained without postulating any induced variations in adsorbate-adsorbate lateral interactions, by assuming the substrate to be heterogeneous. On the basis of our results, we concur

with the view of Ross and Olivier (2), later on shared by deBoer (29), that surface heterogeneity does influence the two-dimensional critical temperature.

To the authors' knowledge, this is the first direct and systematic approach where the effect of surface heterogeneity on the two-dimensional critical temperature of condensation has been reported. However, the exact mechanism by which this influence is brought out is open to speculation. Steele and Karl (17) suggest that the magnitude of potential barriers to translation across the surface affects the configurational properties of the interacting adsorbed atoms and hence  $T_{2C}$ . Or expressed another way, heterogeneity reduces the effective interaction energy (as measured by  $\alpha$ ) and, thus,  $T_{2C}$ , by causing the molecules to adsorb at positions other than those for the optimum attractive interaction. Steele and Karl reported that  $T_{2C}/T_{3C}$  is less for Ne than for Ar or Kr on Graphon and concluded that this is a result of the larger potential barrier to surface translation for Ne compared to Ar and Kr. In this study, gasification of the graphitized carbon blacks will have increased the width and depth of crystallite boundaries and enlarged the diameter and depth of point defects in the basal plane of the crystallites. Therefore, gasification is expected to increase the magnitude of the potential barriers for the translation of Xe across the surface. Following the reasoning of Steele and Karl, gasification of the samples should then result in a decrease in  $T_{2C}$  for Xe, which is found to be the case.

On the basis of the computed model isotherms, Ross and Olivier (2) have predicted that both the shape and slope (and, hence the two-dimensional critical temperature) of the  $W$  vs.  $\theta$  plots should change with surface heterogeneity. However, the model isotherms were derived on the assumption of random distribution of energy sites on the surface. This might be true in the case of the unactivated graphitized carbon blacks. However, in the case of the activated samples, it is known that most of the active sites are not isolated and randomly scattered about the surface but rather grouped together in patches at the edges of the graphite planes (30).

The authors realize that it would have lent

further support to their results if the phenomenon of two-dimensional condensation could have been confirmed experimentally at temperatures less than the observed two-dimensional critical temperature. However, the low vapor pressure of Xe at such low temperatures [for example,  $4.8 \times 10^{-6}$  Torr at 60°K (31)] did not permit such an attempt, at least with the equipment used in the present investigation.

#### ACKNOWLEDGMENTS

The authors wish to thank Professor W. A. Steele for very useful discussions and interest in this study. The research was supported by the AEC on Contract Number AT(30-1)-1710.

#### REFERENCES

1. DEBOER, J. H., "The Dynamical Character of Adsorption," Clarendon Press, Oxford, (1953).
2. ROSS, S. AND OLIVIER, J. P., "On Physical Adsorption," Interscience, New York, (1964).
3. YOUNG, D. M. AND CROWELL, A. D., "Physical Adsorption of Gases," Butterworths, London, (1962).
4. HILL, T. L., *J. Chem. Phys.* **14**, 441 (1946).
5. DEVONSHIRE, A. F., *Proc. Roy. Soc.* **A163**, 132 (1937).
6. LENNARD-JONES, J. E. AND DEVONSHIRE, A. F., *Proc. Roy. Soc.* **A163**, 53 (1937).
7. ROSS, S. AND WINKLER, W., *J. Colloid Sci.* **10**, 319 (1955).
8. ROSS, S. AND WINKLER, W., *J. Colloid Sci.* **10**, 330 (1955).
9. McALPIN, J. J. AND PIEROTTI, R. A., *J. Chem. Phys.* **41**, 68 (1964).
10. CLARK, H., *J. Phys. Chem.* **59**, 1068 (1955).
11. LAINE, N. R., VASTOLA, F. J., AND WALKER, P. L., JR., *J. Phys. Chem.* **67**, 2030 (1963).
12. GRIFFITHS, D. W. L., THOMAS, W. J., AND WALKER, P. L., JR., *Carbon* **1**, 515 (1964).
13. WALKER, P. L., JR. AND JANOV, J., *J. Colloid and Interface Sci.* **28**, 449 (1968).
14. WALKER, P. L., JR., AUSTIN, L. G. AND THIETJEN, J. J., "Chemistry and Physics of Carbon," (P. L. Walker, Jr., ed.) Vol. 1, pp. 327-365. Marcel Dekker, New York.
15. COCHRANE, H., WALKER, P. L., JR., DIETHORN, W. S., AND FRIEDMAN, H. C., *J. Colloid and Interface Sci.* **24**, 405 (1967).
16. HILL, T. L., "Advances in Catalysis," Vol. 4, p. 211, Academic Press, New York, (1952).
17. STEELE, W. A. AND KARL, R., *J. Colloid and Interface Sci.* **28**, 397 (1968).

18. PIERCE, C. AND EWING, B., *J. Am. Chem. Soc.* **84**, 4070 (1962).
19. AVGUL, N. N., KISELEV, A. V., AND LYGINA, I. A., *Kolloidn. Zh.* **25**, 513 (1961).
20. DEBOER, J. H., "Advances in Catalysis," Vol. 8, p. 17, Academic Press, New York, (1956).
21. MAGNUS, A., *Z. Physik. Chem.* **A142**, 401 (1929).
22. MAGNUS, A., *Trans. Faraday Soc.* **28**, 386 (1932).
23. MIGNOLET, J. C. P., *Rec. Trav. Chim.* **74**, 701 (1955).
24. EHRLICH, G. AND HUDDA, F. G., *J. Chem. Phys.* **30**, 493 (1959).
25. SINANOGLU, O. AND PITZER, K. S., *J. Chem. Phys.* **32**, 1279 (1960).
26. MCLACHLAN, A. D., *Mol. Phys.* **7**, 381 (1964).
27. DEBOER, J. H. AND KRUYER, S., *Trans. Faraday Soc.* **54**, 540 (1958).
28. DEBOER, J. H. AND BROEKHOFF, J. C. P., *Proc. Koninkl. Nederl. Akad. van Wetenschappen*, Amsterdam, Series **B70**, 333 (1967).
29. DEBOER, J. H., "On Physical Adsorption," p. vii, Interscience, New York, (1964).
30. HEALEY, F. H., YU, YUNG-FANG, AND CHESICK, J. J., *J. Phys. Chem.* **59**, 399 (1955).
31. HEUSSE, W. AND OTTO, J., *Z. Tech. Physik* **13**, 277 (1932).