
ARGON AND NITROGEN ADSORPTION ON GRAPHITE AT HIGH TEMPERATURES

Eduardo Jorge BOTTANI, Jorge Luis LLANOS and Lydia Ethel CASCARINI DE TORRE

*Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA),
Facultad de Ciencias Exactas, UNLP, Casilla de Correo 16, Suc. 4 RA-1900, La Plata,
Argentina*

Received April 10, 1990

Accepted May 29, 1990

Nitrogen and argon adsorption on two graphites differing in their surface homogeneity was studied in a wide range of temperatures (77.5 K up to 183.2 K). The experimentally determined entropy of the adsorbed phase and isosteric heat of adsorption were analyzed. The Hill-de Boer adsorption isotherm was employed to calculate the apparent two-dimensional critical temperature. The behaviour of the adsorbed film was analyzed to explain the influence exerted upon it by temperature and surface homogeneity.

Surface heterogeneity can be attributed to energetic and structural (porosity) origins¹. In order to estimate the degree of energetic surface heterogeneity several methods have been proposed². In a previous paper³, the authors employed the apparent two-dimensional critical temperature as a parameter to estimate the surface homogeneity of several characterized solid surfaces at 80.2 K. However the characterization of a surface, inferred from physical adsorption data naturally depends on the properties of the adsorbed film, such as the adsorbate molecule used, the temperature conditions and the surface coverage range analyzed. For these reasons it is considered important to compare surface heterogeneity determinations using a wide range of temperature and surface coverage including adsorbates with different molecular properties.

In this paper a series of adsorption isotherms of nitrogen and argon on two different graphites were measured in the temperature range 77.5 K to 183.2 K. The state of the adsorbed phase was determined for different surface coverages. The isotherms obtained comprise a wide range of relative strength of vertical and lateral interactions.

The Hill-de Boer model was applied to all isotherms to estimate the interaction parameters and to calculate the apparent two-dimensional critical temperature (T_{2c}^*), which is a measure of surface heterogeneity³. Isosteric heats of adsorption and entropy were determined by methods already described⁴. The state of the adsorbed phase and the influence of temperature and surface heterogeneity is discussed

through the use of the entropy/heat of adsorption-coverage profiles. Some characteristics of the isosteric heats of adsorption are also discussed.

EXPERIMENTAL

The adsorption isotherms were determined in a volumetric apparatus following the technique described elsewhere³. The samples employed in this work were: Sterling MT-FF and "National" graphite. Both of them were previously described and characterized³: Sterling MT-FF is a sample graphitized at 1 300°C and very homogeneous while "National" graphite is a very heterogeneous sample obtained by grinding a spectroscopically pure graphite bar.

Temperature was measured with a digital platinum thermometer previously calibrated against an oxygen vapour pressure one. The temperature could be varied in the range 80–273 K ± 0.2 K using a cryostat constructed in our Laboratory following a design of A. Thomy.

The BET monolayer capacities of the graphite samples were determined at 77.5 K and these values were used to calculate the surface coverage.

Experimental errors are 1% for entropy and isosteric heat of adsorption, respectively, and 2 K for T_{2c}^* .

RESULTS AND DISCUSSION

Measured adsorption isotherms for nitrogen and argon are shown in Figs 1–4. Reversible behaviour was observed at all temperatures and surface coverages. In Figs 5–8, the isosteric heats of adsorption are represented as function of surface coverage and some characteristics of these curves will be considered. For example argon adsorbed on Sterling MT-FF shows different behaviour at different tempera-

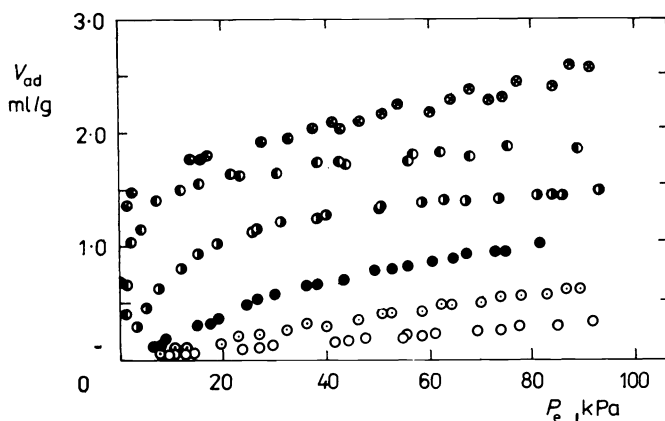


FIG. 1

Nitrogen/Sterling MT-FF adsorption isotherms: ○ 182.3 K, ○ 163.2 K, ● 143.2 K, ● 123.2 K, ● 103.2 K, ● 93.2 K

ture (Fig. 5). At 98.2 K, the isosteric heat decreases with surface coverage while at 133.2 K the isosteric heat increases with coverage. At 113.2 K, it shows the effect of residual heterogeneity and then, at greater coverages, lateral repulsions predominate.

However the system Ar/"National" graphite displays a different behaviour (see Fig. 6). This very heterogeneous graphite has particles with a great proportion of

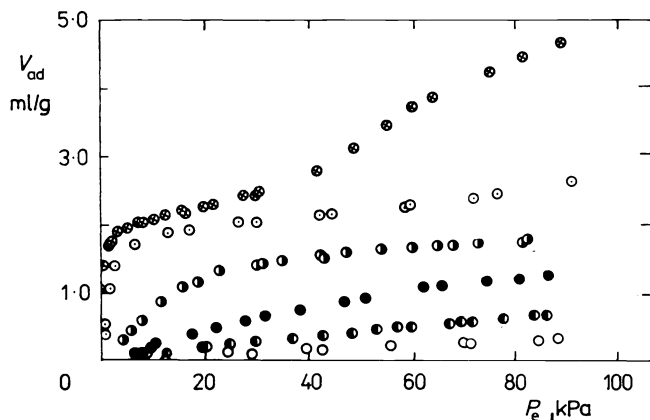


FIG. 2

Argon/Sterling MT-FF adsorption isotherms: ○ 183.2 K, ○ 163.2 K, ● 143.2 K, ● 123.2 K, ● 103.2 K, ⊕ 93.2 K

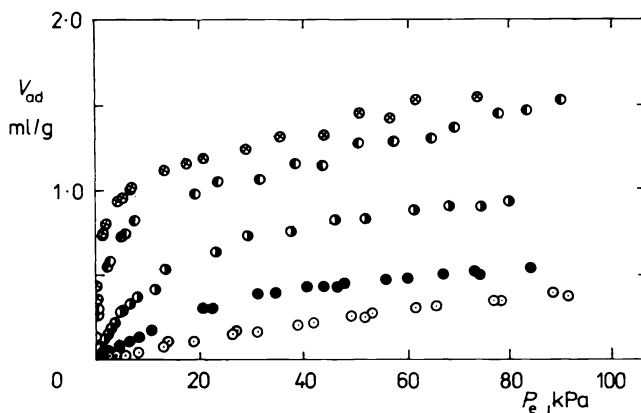


FIG. 3

Nitrogen/"National" graphite adsorption isotherms: ○ 163.2 K, ● 143.2 K, ● 123.2 K, ● 103.2 K, ⊕ 93.2 K

edges and fractures. At all temperatures studied this sample appears as heterogeneous. Thus at 98.2 K, the isosteric heat that initially diminishes is practically constant (10.7 kJ/mol) for coverages between 0.36 and 0.6, then it abruptly decreases and becomes constant again (3.6 kJ/mol). The isosteric heat corresponding to the second horizontal part is 34% of the first plateau. This ratio is in good agreement with the value quoted by Thomas et al.⁵ (40%) for the heat of adsorption based on a two-surface analysis of adsorption data. In consequence, the first part of the curve could be in principle assigned to preferential adsorption on edges and the last one to adsorption on the plane part of the surface. In this system the increase of isosteric heat due to lateral interactions is not observed because the solid strongly perturbs them, consequently the vertical ones predominate.

From the isosteric heat curves, different degrees of surface heterogeneity could be inferred even for the same solid. This fact can be explained if the effect of temperature upon adsorbate mobility and interactions is considered. In effect, an increase in temperature implies greater mobility of adsorbed molecules and an increase in lateral interactions which can be interpreted as an indication of a homogeneous surface. The opposite phenomenon operates with a decrease in temperature, therefore the same surface can be qualified as homogeneous or heterogeneous according to the experimental conditions under which the isotherms were obtained.

The isosteric heat curves for the system nitrogen/Sterling MT-FF are shown in Fig. 7 and some interesting features shall be described. As it can be expected, at 86.8 K, the isosteric heat tends to 5.4 kJ/mol for coverages greater than one. This value is very close to the vaporization enthalpy of liquid nitrogen (5.56 kJ/mol).

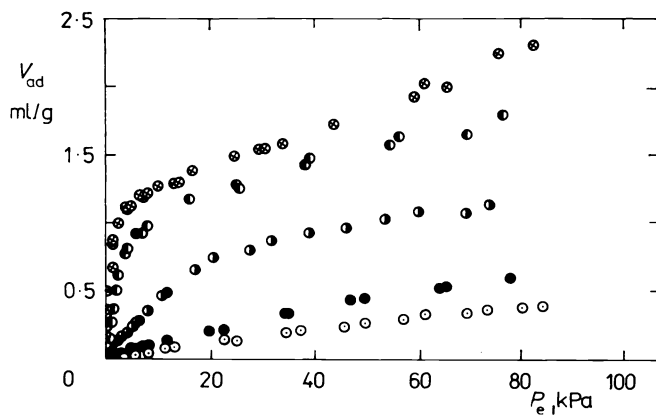


FIG. 4

Argon/"National" graphite adsorption isotherms: ○ 163.2 K, ● 143.2 K, ● 123.2 K, ● 103.2 K, ⊕ 93.2 K

On some curves, a local maximum appears at decreasing surface coverages with increasing temperature. In a previous study⁶, a peak was observed for this system at 78.9 K and for surface coverage ca 1, this peak indicates the end of a net adsorption in the first layer (statistical monolayer capacity) and the beginning of a net multilayer adsorption.

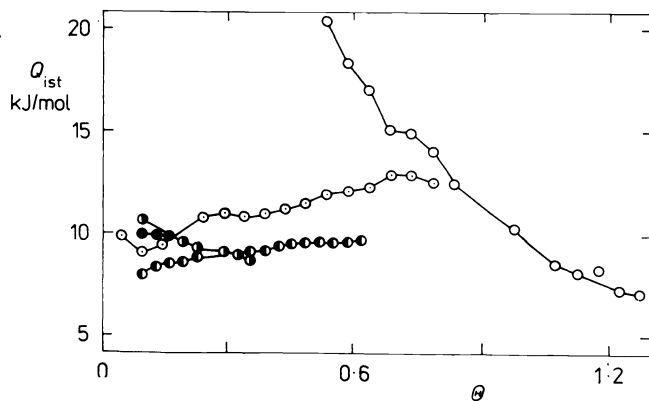


FIG. 5

Argon/Sterling MT-FF isosteric heats in dependence of surface coverage: ○ 98.2 K, ○ 113.2 K, ● 133.2 K, ● 153.2 K, ● 173.2 K

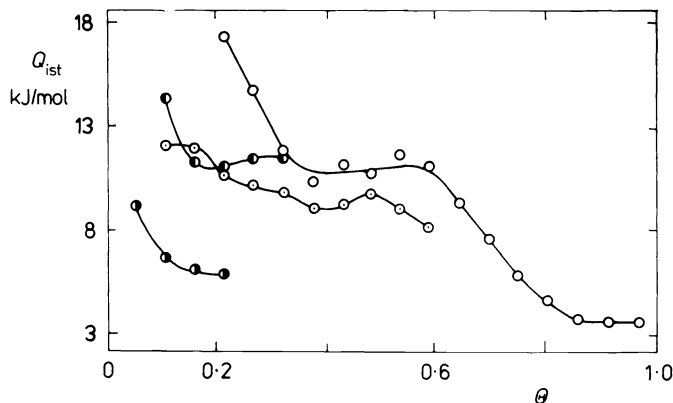


FIG. 6

Argon/"National" graphite isosteric heats in dependence of surface coverage: ○ 98.2 K, ○ 113.2 K, ● 133.2 K, ● 153.2 K

In the present study, the maximum observed can not be explained in the same way, furthermore it is interesting to note that there are two intermediate temperatures where the peak does not appear, instead an initial decrease in the isosteric heat is observed.

The absence of the peak can be due simply to the fact that it is located outside the available experimental range which is limited by the shape of the isotherms⁴.

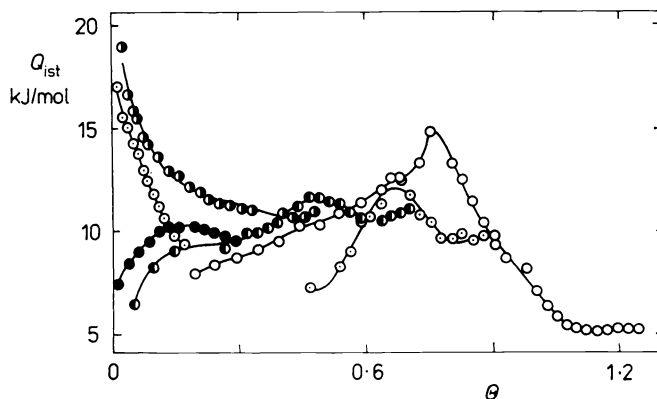


FIG. 7

Nitrogen/Sterling MT-FF isosteric heats in dependence of surface coverage: \oplus 86.8 K, \circ 98.2 K, \odot 113.2 K, \bullet 133.2 K, \ominus 153.2 K, \bullet 173.2 K

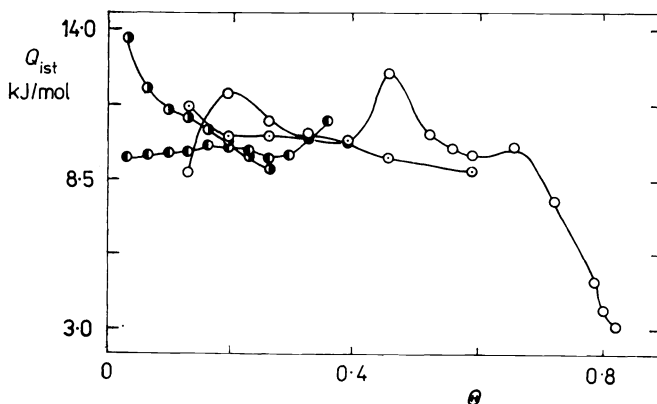


FIG. 8

Nitrogen/"National" graphite isosteric heats in dependence of surface coverage: \circ 98.2 K, \odot 113.2 K, \bullet 133.2 K, \ominus 153.2 K

However the logical sequence of peak location would indicate that, if it exists, it should be observed within the range of surface coverages analyzed.

This behaviour can be explained by a rearrangement caused by a change in the relative strength of lateral and vertical interactions, this rearrangement should be associated with the different orientations that the nitrogen molecule can adopt in respect to the surface.

In order to confirm this hypothesis nitrogen cross-sectional areas were calculated⁶ taking as reference the value assigned to argon (0.136 nm^2). In the first approximation, it is possible to assign three different extreme orientations to the adsorbed nitrogen molecules on the surface. Molecules can lie flat, perpendicular or freely rotating over the surface. The values obtained are shown in Table I. Up to 113.2 K the values are equal to the standard value (0.162 nm^2), then as the temperature increases a transition begins. At 123.2 K the value corresponds to nitrogen molecules freely rotating (0.156 nm^2) over the surface. As the temperature increases, the proportion of molecules laying flat takes the values 45% at 143.2 K , 21% at 163.2 K and 38% at 183.2 K . Thus at 143.2 and 183.2 K a great proportion of molecules lie flat and their vertical interactions (adsorbate-adsorbent) are much more important than the lateral ones, producing a decreasing of the isosteric heat with coverage and indicating surface heterogeneity. At 163.2 K , 21% of the molecules lay flat so lateral interactions (adsorbate-adsorbate) are more important and the curve shows a maximum. All these facts support the idea that the proposed rearrangement in the adsorbed film is taking place. This proposed rearrangement will be further discussed when T_{2c}^* values are considered.

For the system nitrogen/"National" graphite only at the lowest temperature, the peak is observed (Fig. 8) because the solid strongly perturbs lateral interactions as it could be expected from its surface heterogeneity.

More evidence about the behaviour of the adsorbed film can be obtained from the differential entropy of the adsorbed phase. It was calculated following the method previously described⁴. In Figs 9 and 10 the entropy curves are shown. The corresponding curves for nitrogen are represented in Figs 11 and 12. In all cases the, van der Waals model with one and two degrees of rotational freedom was taken as reference.

TABLE I
Nitrogen cross-sectional area for adsorption on Sterling MT-FF

$T, \text{ K}$	77.5	80.4	123.2	143.2	163.2	183.2
$\sigma, \text{ nm}^2$	0.163	0.166	0.1596	0.144	0.133	0.141

The behaviour of argon and nitrogen adsorbed films will be discussed using their differential entropies. At 98.2 K the entropy of argon adsorbed on "National" graphite is constant for coverages between 0.4 and 0.6 and the experimental value is very close to the theoretical one. This could correspond to argon condensation on the edges and fractures of this graphite particles in agreement with what was

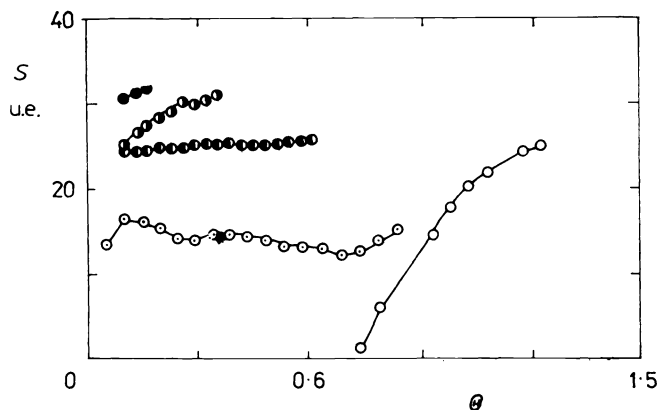


FIG. 9

Argon/Sterling MT-FF entropy in dependence of surface coverage: ○ 98.2 K, ⊙ 113.2 K, ● 133.2 K, ⊙ 153.2 K, ● 173.2 K

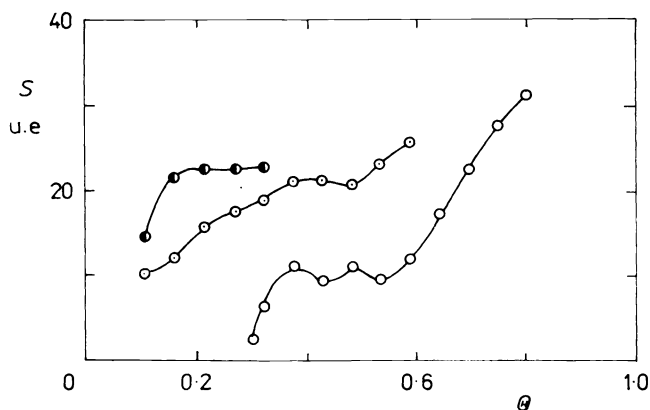


FIG. 10

Argon/"National" graphite entropy in dependence of surface coverage: ○ 98.2 K, ⊙ 113.2 K, ● 133.2 K

said for the isosteric heat; however over the Sterling MT-FF, at the same temperature and at the same surface coverages, the argon molecules tend to delocalization. On the other hand, at low surface coverages the argon molecules are localized on both solids due in part to temperature effects and to surface heterogeneity.

At 113.2 K, the experimental entropy of argon on Sterling MT-FF is very close to the theoretical curve up to surface coverages near to 0.3, then the adsorbate

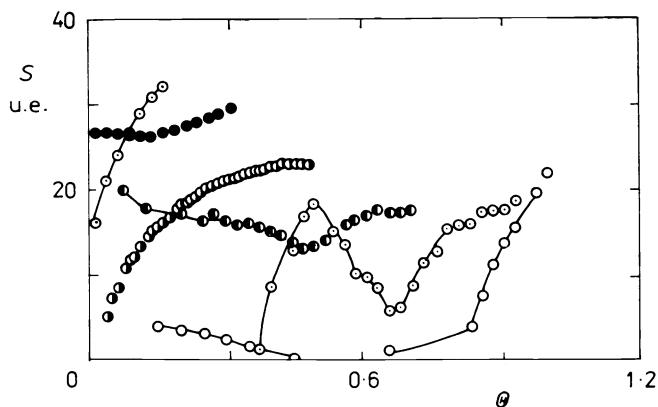


FIG. 11

Nitrogen/Sterling MT-FF entropy in dependence of surface coverage: \oplus 86.8 K, \circ 98.2 K, \circ 113.2 K, \bullet 133.2 K, \bullet 153.2 K, \bullet 173.2 K

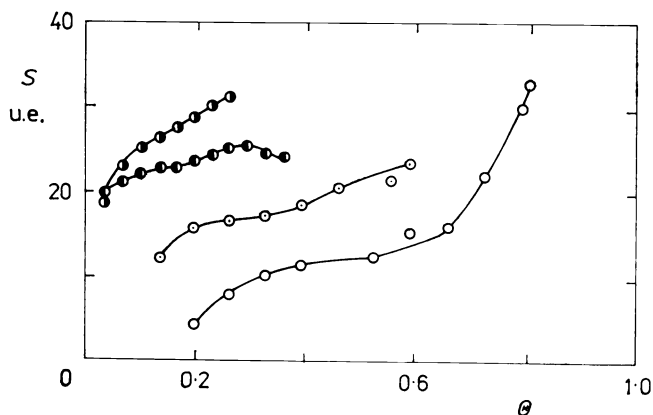


FIG. 12

Nitrogen/"National" graphite entropy in dependence of surface coverage: \circ 98.2 K, \circ 113.2 K, \bullet 133.2 K, \bullet 153.2 K

molecules acquire "supermobility". Over "National" graphite the experimental curve indicates a tendency to delocalization and in the range of coverages between 0.4 and 0.5, the entropy is practically constant. This plateau is smaller than the observed at 98.2 K on the same surface. At greater temperatures the system argon/"National" graphite shows even smaller restrictions in adsorbate mobility and finally it behaves as "supermobile". Argon adsorbed on Sterling MT-FF shows "supermobility" at 133.2 K and higher temperatures.

The entropy curves of nitrogen show a more complicated picture. At most temperatures studied "National" graphite imposes more restrictions than Sterling MT-FF in adsorbate mobility. This is to be expected since "National" graphite is more heterogeneous than the Sterling MT-FF, however at 113.2 and 133.2 K this behaviour is reversed, and the mobility of the adsorbed nitrogen molecules is greater in "National" graphite than in Sterling. This reinforces the rearrangement model previously proposed in the discussion of isosteric heats results.

T_{2c}^* values were also calculated for each experimental isotherm (Table II). Its use as a parameter to measure the surface heterogeneity degree was described in a previous paper³. It must be pointed out that the greater values of T_{2c}^* correspond to the more homogeneous surfaces. T_{2c}^* values obtained for nitrogen on Sterling MT-FF show an abrupt diminution between 102.3 and 123.2 K and then they become constant. This diminution is related to the change in the structure of the adsorbed phase previously discussed. In fact the T_{2c}^* value can be altered in respect

TABLE II
Apparent two-dimensional critical temperature. Maximum error in temperature quotient is ± 0.02

Adsorbate	T, K	T_{2c}^*/T_{3c}	
		National	Sterling MT-FF
Argon	103.2	0.16	0.47
	123.2	0.25	0.47
	143.2	0.26	0.45
	163.2	0.21	0.39
	183.2	—	0.44
Nitrogen	103.2	0.09 ^a	0.50
	123.2	0.30	0.35
	143.2	0.33	0.35
	163.2	0.58	0.32
	183.2	—	0.33

^a Best fit with few experimental points.

to its ideal value by a change in the interaction parameter that necessarily implies a change in the cross-sectional area of the adsorbate.

The rearrangement of the adsorbed phase detected for the system nitrogen/Sterling MT-FF was confirmed through entropy/isosteric heat curves, nitrogen cross-sectional areas and apparent two-dimensional critical temperature. This phenomenon occurring in the adsorbed phase must be considered as a property of the adsorbate with some contribution of the adsorbent degree of heterogeneity. This idea is in agreement with the fact that when the surface is homogeneous it enables a full development of lateral interactions which are a function of the nature of the adsorbed molecules.

One interesting fact is that this rearrangement seems to begin at a temperature close to the three-dimensional critical temperature of nitrogen (126 K). At this point a permanent gas is being adsorbed which is quite different from a vapour.

Another conclusion that can be derived from the analysis of the entropy curves is that the effects of surface heterogeneity seems to be better detected by nitrogen molecules because restrictions in the mobility imposed by the solid are still shown at high temperatures.

Finally it must be stressed that if surface heterogeneity were to be evaluated from argon adsorption isotherms on both solids the conclusion would be that Sterling MT-FF is more homogeneous than "National" graphite but if only one or two of the highest temperature isotherms were selected to make the study nothing could be said because the behaviour of the adsorbate is the same on both solids. This fact makes evident that a complete set of isotherms must be analyzed to define the relative heterogeneity of two or more surfaces.

This project was financially supported by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC). EJB is researcher of the CIC.

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