NITROGEN CROSS-SECTIONAL AREA ON STANDARD GRAPHITE

L. E. Cascarini de Torre, J. L. Llanos and E. J. Bottani

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA),
Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 1900 La Plata, Argentina

Nitrogen physical adsorption at 77·5 and 80·4 K on a standard graphite was studied with the purpose to analyze adsorption models and to determine nitrogen cross-sectional areas for each model. With this intention different models, such as Van der Waals, Langmuir, and BET, which describe the adsorption process at different surface coverages were employed. Molar differential entropies and isosteric heats of adsorption were calculated. A two-dimensional phase transition was confirmed. Adsorbed molecule cross-sectional areas were determined at different surface coverages, by direct comparison with that corresponding to argon. The values obtained varied in a wide range (0·135 to 0·166 nm^2) depending on surface coverage.

The problem of determining the actual value of nitrogen cross-sectional area has acquired a great importance in the last years. A lot of scientific work has been done over this subject[1-6] and the IUPAC has pointed out the importance of this problem[7]. It has been demonstrated undoubtedly that the cross-sectional area of nitrogen can vary widely. Its variations are mainly function of surface heterogeneity, preferential orientations on the solid surface and interactions with surface impurities such as hydroxyl groups.

One important aspect to be clarified, previously to the adoption of any cross--sectional area value, is the adsorbed phase state. This depends on the solid surface, temperature and in this paper it is emphasized the dependence on surface coverage and on phase transition. The adsorbed film state can be inferred from the adsorption model and from entropy curves too. In this work, nitrogen adsorption isotherms are described by three different models depending on surface coverage. The coverage regions in which each model is obeyed are in agreement with the behaviour showed by the entropy curve.

EXPERIMENTAL

The adsorption isotherms were obtained over Sterling MT-FF graphite, graphitized at 3 100°C. Its specific (BET) surface area was 8·9 m^2/g. The temperatures studied were 77·5 and 80·4 K. The gases employed were of high purity and transferred to the equipment under high vacuum. The sample was outgased at 350°C in high vacuum during an average period of 10 hours. The isotherms were determined in a conventional volumetric equipment, constructed from Pyrex glass.

Pressures were measured with three manometers depending on the pressure range: up to 1·33 kPa an MKS Baratron pressure transducer; between 1·33 and 10·6 kPa a McLeod and from 7·98 kPa up to 101 kPa a National semiconductor pressure transducer was used.

All temperatures were measured using a digital thermometer with a Pt (Pt-100 DIN) head sensor, previously calibrated against a vapour pressure thermometer. In the analysis of argon isotherms its saturation tension in the solid state was employed. For each experimental temperature its value was calculated using the following relation[8]:

$$\log P = -0.05223 X/T + Y, \qquad (1)$$

where $X = 7\,814.5$, $Y = 7.5741$, and P is in Torrs (1 Torr = 133·322 Pa). This equation is valid between 65 K and 84 K.

All data were processed using an HP-1001/F minicomputer, and programs were written in FORTRAN-4X.

Standard error analysis showed that the error in pressure was ± 0.3 Pa, the maximum error in the adsorbed volume was less than 0·3% and 1% in entropy values.

RESULTS AND DISCUSSION

The adsorption isotherms are shown in Figs 1 and 2. The reversibility of the adsorption process was confirmed by measuring the desorption points at different surface coverages.

Nitrogen adsorption isotherm at 77·5 K shows a little step at a relative pressure near 0·01. This system was also studied by Rouquerol et al.[9−12] employing adsorption microcalorimetry. They found the same step and assigned it to the transformation of a hypercritical two-dimensional gas into a two-dimensional solid. This solid phase is in registry with the adsorbent structure. The cross-sectional area of nitrogen molecule was taken, at this conditions, by Rouquerol et al.[10] as 0·1575 nm².

For both temperatures, the adsorbed phase follows at low surface coverages the Van der Waals model, then the Langmuir one (between 0·6 and 0·9 of a monolayer) and finally, at greater surface coverages the BET model (coverages between 0·9 up to 1·5 of a monolayer). All models, in their linear form, were fitted to experimental data using the least squares method. The correlation coefficients obtained were in all cases greater than 0·99. It must be pointed out that a good fit of experimental data by any model does not mean that its assumptions are valid. The aim of this kind of analysis is to obtain the parameters of the model such as the monolayer capacity, and to extract useful information from them.

Molar differential entropies were calculated to confirm the adsorbed phase behaviour. The method employed was described elsewhere[13−15] and the corresponding curves are shown in Fig. 3. The experimental entropy, calculated from isosteric heat, is compared with that which corresponds to a two-dimensional Van der Waals gas with a loss of one or two rotational degrees of freedom. In the region of low surface coverages, nitrogen behaves as a "supermobile" two-dimensional gas with a maximum near 0·2 of a monolayer. Then it decreases and reaches its minimum

value at 0·6 of a monolayer. Here nitrogen molecule is nearly localized. It must be noted that the surface coverage where nitrogen molecule is localizing, is coincident with that of the phase transition.
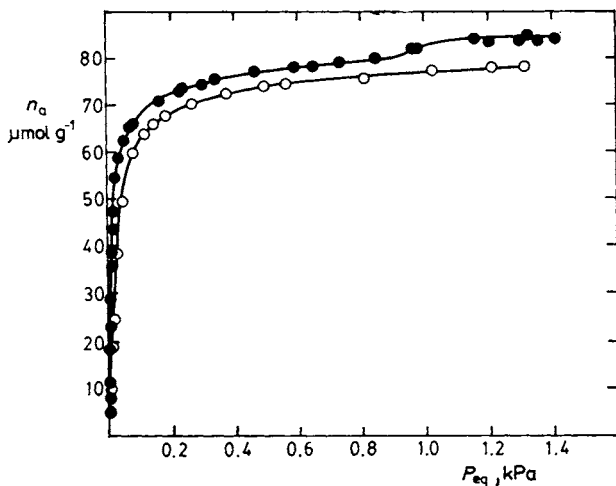

FIG. 1

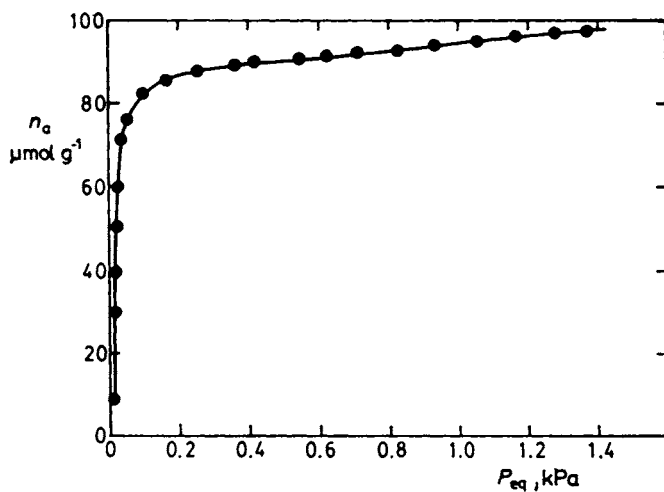Nitrogen adsorption isotherms on graphite; ● 77·5 K, ○ 80·4 K

FIG. 2

Argon adsorption isotherm on graphite; $T = 77 \cdot 5$ K

To obtain the entropy curves, two adsorption isotherms must be employed. The temperature difference between these isotherms cannot exceed 10 K to be sure that the adsorption enthalpy value remains constant. The entropy curve that results in this way corresponds to an intermediate state of the adsorbed phase. Then, the behaviour shown by this curve is an "average" between the employed temperatures. Despite a little temperature difference between both isotherms (77·5 and 80·4 K) the experimental error, less than 0·3%, enables the determination of both the isosteric heat and the entropy with errors less than 1%.

The isosteric heats of adsorption were calculated employing the Clausius–Clapeyron equation as a function of surface coverage, and a sharp maximum is obtained when the statistical monolayer is completed. At lower surface coverages (c. 0·4) a local minimum is observed (see Fig. 4). This minimum corresponds to the begining of the localization of the adsorbed phase as can be seen in the entropy curve. At this point, the Langmuir model begins to describe the adsorbed phase state.

At low coverages the Van der Waals model is followed. The mean orientation of nitrogen molecule on the solid surface was calculated by the method of Ross and Olivier[16] and the result was that the adsorbed molecules rotate freely on the surface. This method implies a theoretical evaluation of the relation a/b, where a and b are the two-dimensional parameters of the Van der Waals model. To do so, molecular parameters such as polarizations, diameters, etc., in different molecular orientations on the surface must be known, in our case the values given by Ross and Olivier[16] were used. These theoretical values are compared with the experimental one. From this comparison, the molecular orientation in respect to the surface can
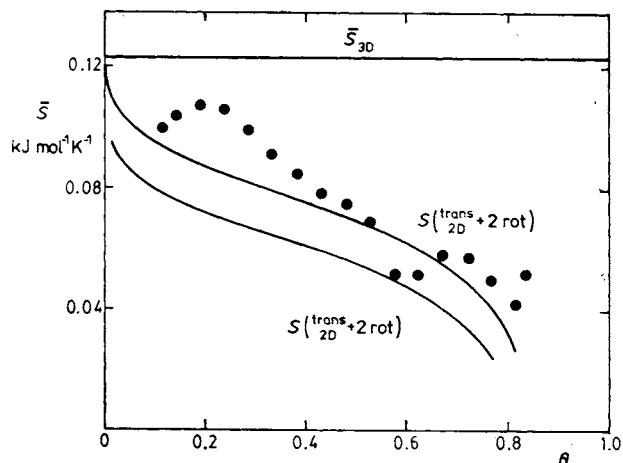

FIG. 3

Molar differential entropy for nitrogen on graphite; $T_m = 78·9$ K

be inferred. As was said above, at greater coverages the Langmuir model is obeyed and then in the multilayer region, the BET model describes the adsorption process.

The monolayer capacities were calculated for the three models. Within the coverage region where the Van der Waals equation is satisfied, V_b was determined; in this situation, V_b is the monolayer capacity when the adsorbed film behaves as a two-dimensional Van der Waals gas[16] (Table I).

Argon adsorption isotherm was measured to obtain its monolayer capacities, at different surface coverages. Nitrogen monolayer capacities were compared with those corresponding to argon. All values are summarized in Table I.

To obtain the actual value of nitrogen cross-sectional area at different coverages, we have chosen argon as reference because it has no different orientations on the solid surface. The value[1] taken was 0.136 nm^2.

The relationship between argon and nitrogen cross-sectional areas is defined by:

$$a_m(N_2) = a_m(Ar)\left[V_m(Ar)/V_m(N_2)\right], \qquad (2)$$

where $a_m(N_2)$ and $a_m(Ar)$ are respectively nitrogen and argon cross-sectional areas, and $V_m(Ar)$ and $V_m(N_2)$ are argon and nitrogen monolayer capacities.

We have related the monolayer capacities of nitrogen and of argon in different regions of surface coverage studied. Van der Waals, Langmuir or BET monolayer capacities, for each gas, are compared within the surface coverage region where each equation fits to experimental data. In Table II, the values for both temperatures
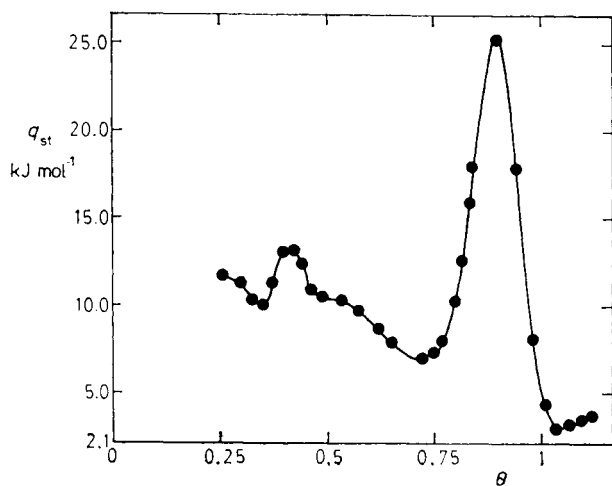

FIG. 4

Isoteric heat of adsorption of nitrogen on graphite; $T_m = 78.9$ K

studied are given. It can be seen that for low surface coverages, nitrogen molecule presents its classical cross-sectional area. This value, deduced from the density of the liquid, assumes that the molecules are spherical. This result is in agreement with the adsorbed phase behaviour previously mentioned. As the surface coverage increases the adsorbed molecules display a cross-sectional area, 0.1575 nm^2 at 77·5 K, which is in accordance with that proposed by Rouquerol[10]. At 80·4 K, the Langmuir cross-sectional area has the standard value. This may be explained if one keep in mind the greater adsorbate mobility at this experimental condition in respect to 77·5 K. In the multilayer region the cross-sectional area found corresponds to a solid packing $(0.138$ nm^2 as calculated by Voet[3]$)$ of nitrogen molecules on the solid.

From the cross-sectional area values obtained it can be seen that the adsorbed film density increases with surface coverage. This effect is clearly shown at 77·5 K where it occurs in three different stages. At 80·4 K only two stages are well developed. The main difference between both temperatures is that at 77·5 K the film performs a phase transition just before monolayer completion. At 77·5 K in the adsorbed phase, when Langmuir equation is satisfied, nitrogen molecule is more localized,

TABLE I

Argon and nitrogen statistical monolayer capacities (in μmol g^{-1}) deduced from different adsorption models

T	Argon			Nitrogen		
K	V_m(BET)	V_m (Langmuir)	V_b	V_m(BET)	V_m (Langmuir)	V_b
77·5	9·11	9·38	11·2	9·15	8·13	9·33
80·4	9·33	9·46	11·2	9·29	7·95	9·20

TABLE II

Nitrogen cross-sectional areas (in nm^2) deduced from Eq. (2)

T, K	a_m(BET)	a_m(Langmuir)	a_m(Van der Waals)
77·5	0·135	0·157	0·163
80·4	0·137	0·162	0·166

and this situation is responsible for instabilities in the adsorbed phase as the surface coverage increases. So a phase transition is necessary to stabilize the adsorbate. At 80·4 K, the localization of the adsorbed phase is weaker due to the greater kinetic energy that possess the adsorbed molecules. In this situation, the instabilities, mentioned above, are not present or are less important and phase transition does not appear. The adsorbed layer compression produces a great variation in nitrogen cross-sectional area values $\left(\text{c. } 21\%\right)$.

In this paper, we have shown the different adsorbed layer states and obtained the actual cross-sectional area of nitrogen at different degrees of surface coverage. In this way, differences found by different authors are explained. It is important to remark that the experimental isotherms employed here were measured over a very homogeneous graphite (Ross and Olivier's heterogeneity parameter greater than 1 000). In previous works, the authors have shown the influence that surface homogeneity excercises over the adsorbed phase behaviour[17]. More experimental work is being conducted at present, in order to show the dependence of nitrogen cross-sectional area with surface degree of heterogeneity.

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