

Energetical aspects of N₂ and Ar adsorption: specific adsorption, two-dimensional phase changes and adsorption in micropores

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Abstract - This paper reports information obtained from experiments of high resolution adsorption microcalorimetry of N₂ or Ar at 77 K, which illustrate a few ideas strongly supported by A.V. Kiselev. The interest of comparative adsorption of N₂ and Ar (as complementary probes) is shown in the case of the following adsorbents : hydroxylated non-microporous oxides (amorphous or crystalline, giving rise to "specific" adsorption), graphite and boron nitride (whose homogeneity leads to detectable two-dimensional phase changes) and microporous carbons (giving rise to enhanced "non-specific" adsorbate-adsorbent interactions).

INTRODUCTION

In this paper we wish to present some developments -in the field of N₂ and Ar adsorption at 77 K- of a few ideas formerly supported by A.V. Kiselev.

One of these ideas is the classification of adsorbates and adsorbents after their capacity for "specific" or "non-specific" molecular interactions (ref. 1). The latter generally coincide with the universal dispersion interactions, whereas the specific interactions involve local peculiarities of the electron density distribution. Saturated hydrocarbons and noble gases are supposed to give rise to non-specific interactions only (this being then the case for argon) whereas any molecule with π bonds, or with a permanent dipole or quadrupole moment (like that of nitrogen) is supposed to lead also to specific interactions, provided the adsorbent carries localized polar groups or positive charges.

The surface of the adsorbent may therefore be usefully explored by 2 probe-molecules selected to give rise to similar non-specific interactions (*i.e.* having comparable size, geometry and polarizability) but presenting a great difference in their local electron density distribution : one alkane and a corresponding alcohol, benzene and cyclohexane, nitrogen and argon.

A.V. Kiselev was also convinced that any basic study on the phenomenon of adsorption needed a direct determination of the energies involved and he developed, with his co-workers, several calorimetric devices specially adapted for adsorption studies and allowing to measure either the differential enthalpy of adsorption (ref. 2,3) or the heat capacity of the adsorption system (ref. 4) at temperatures above 150 K.

Finally, he gave a special attention to graphitized carbon surfaces which be considered as the simplest and best model surfaces for non-specific adsorption (ref. 5,6).

We therefore found it interesting to draw benefit from our possibility of carrying out high resolution adsorption microcalorimetric experiments at 77 K (ref. 7), *i.e.* at a temperature which had not been reached in the above works and which had the great advantage of allowing to compare the behaviour of N₂ and Ar at a temperature where a tremendously large amount of work (except in calorimetry) was already available in the litterature.

ENERGETICAL ASPECTS OF SPECIFIC ADSORPTION

Besides their numerous practical applications, oxide surfaces have the great interest of lending themselves to any extent of hydroxylation, crystallinity and microporosity. It follows that compared adsorption of N₂ and Ar may be a useful tool to characterize one such surface. In the case of mesoporous silica gels, adsorption microcalorimetry at 77 K gives striking results, confirming and extending an exploratory work carried out by Aristov and Kiselev (ref. 8) on 2 samples only (silica gel outgassed at 160 and 970°C, respectively) and

by the indirect isosteric method. We could check, indeed, on various silicas (ref. 9, 10) that the curve of differential enthalpy of adsorption of N_2 vs coverage progressively shifts to lower values as the silica is dehydroxylated by a thermal outgassing carried out in successive steps from 150 to 1000°C. From the shift, we may derive a molar enthalpy of "specific" interaction of N_2 with a fully hydroxylated surface which amounts to c.a. $3 \text{ kJ} \cdot \text{mol}^{-1}$. On the other hand, no shift at all is observed in the case of argon, (the enthalpy curve is independent from the extent of dehydroxylation) showing here a clear-cut case of "non-specific" adsorption. This result gives support to the assumption of a statistical orientation of the N_2 molecule in the monolayer (ref. 11), stabilized by the above specific interaction, whereas, following Kiselev's words, "the adsorption of argon is insensitive to ... dehydroxylation" (ref. 8). Nevertheless, we must admit that the discussion on the "true" area covered by one N_2 or Ar molecule in the BET monolayer is not over, mainly because of the lack of independent and "absolute" surface area determinations, also taking into account, if possible, the concepts of fractal geometry. In these conditions, the scientists recently interested in determining a scale of molecular areas of N_2 and Ar on adsorbents of different nature (ref. 12,13) were confined to consider -at least as a provisional reference- the "historical" microcalorimetric determination of Harkins and Jura on an anatase sample (ref. 14), together with the electron microscopic determination of Pickering and Ecstrom on the same sample (ref. 15), although we know that the former experiment was certainly incorrect in its original form (ref. 16) ...

In contrast with the above results, calorimetric determinations show in the case of zirconia (ref. 17) and even more in the case of rutile (ref. 18) that the energy of interaction of argon with the surface *increases* in a measurable extent (+ 24% and + 58%, respectively, at a coverage of 0.25) as the outgassing temperature is raised (from 110 to 500 and from 150 to 400°C, respectively). Although the increase observed in the case of N_2 is much higher (certainly involving both a quadrupolar and an induced dipolar interaction with Zr^{3+} and Ti^{4+} surface cations and, more generally, with the surface crystalline field), Ar therefore shows some sensitivity to the nature of the surface, through induced polar interactions.

A practical application of the specific interactions of N_2 and Ar with a surface is illustrated in Fig. 1, where we plot the derivative enthalpy of adsorption of these gases on a polycrystalline, non-microporous, ZnO sample (kindly supplied by Mr. Fujiwara, from Sakai Chemical Industry Co., Fukushima, Japan, this being the "special sample n° 5905") of c.a. $3.5 \text{ m}^2 \text{g}^{-1}$. The two plateaus observed up to a coverage of c.a. 0.5 suggest adsorption on homogeneous faces of the sample. The much higher value of $\Delta_{\text{ads}} h$ in the case of nitrogen (c.a. 4 times the enthalpy of liquefaction, instead of 2 times in the case of argon) suggests an interaction with a highly polar surface such as the polar hexagonal faces (0001) of the prismatic crystals of ZnO, which, being here outgassed at 450°C, are covered with unscreened Zn^{++} cations. The fact that the plateau is longer in the case of N_2 may be explained by a specific interaction of N_2 with less polar parts of the surface, such as the edges of the basal planes and, possibly also, defects of the crystal which do not induce as high a dipole moment of the Ar molecule as the polar basal faces do. After the above considerations we derive a proportion of 43% polar faces (from the length of the Ar plateau), 10% edges and defects (from the difference between the length of the N_2 and Ar plateaus) and 47% lateral faces (i.e. the rest).

We had formerly used and checked a similar reasoning to determine the proportion of basal planes and lateral surface in the case of kaolinite : a good agreement was found with ionic surfactant adsorption, electron microscopy and image analysis being less reliable (ref. 19).

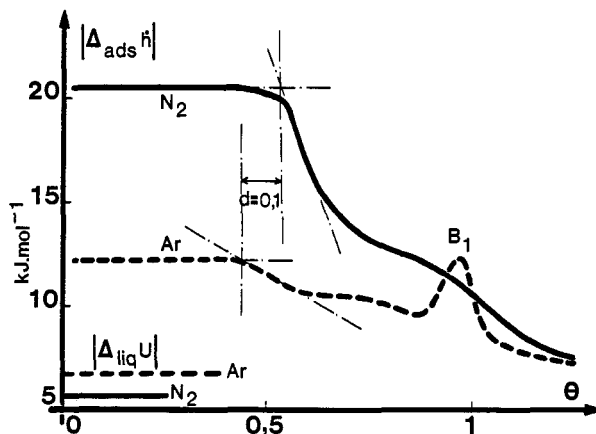


Fig. 1. High resolution differential enthalpy of adsorption of N_2 and Ar on polycrystalline ZnO at 77 K.

ENERGETICAL ASPECTS OF TWO-DIMENSIONAL PHASE CHANGES

A.V. Kiselev considered graphitized carbon black as the best reference sample, in competition with zeolites, to collect adsorption parameters "expressed in terms of absolute quantities, reproducible in any adequately equipped laboratory" (ref. 20). Several teams were indeed able to determine, in these years, a number of superimposable adsorption isotherms of N_2 on various graphitized blacks at 77 K. Nevertheless, it was necessary to wait for the use of high resolution adsorption microcalorimetry (the resolution arising from the use of a quasi-equilibrium procedure (ref. 9)) to detect, at the completion of the monolayer, in these systems often studied in the past, a sudden phase change from a 2D-hypercritical fluid to a 2D-crystal, both for N_2 and Ar (ref. 21). This phase change also results in a sub-step of the adsorption isotherm but which is hardly seen by conventional point by point adsorption volumetry.

We have a very similar phenomenon in Fig. 2, corresponding to adsorption of argon, at 77 K, on a sample of polycrystalline boron nitride of c.a. $14 \text{ m}^2\text{g}^{-1}$, provided by Carbone Lorraine. The phase change in question gives rise, at point B_1 , both to a weak sub-step in the adsorption isotherm and to a sharp peak, much easier to detect, in the enthalpy curve. The "waves" visible in the latter curve and corresponding to the successive completion of the 2nd and 3rd layer had already been seen by Pierotti (ref. 22), who used the isosteric method, but the peaks (in B_1 , already commented on, and in B_2) needed high resolution adsorption microcalorimetry to be detected. The analysis of the enthalpy curve allows to derive the molar enthalpy of adsorption of Ar at zero coverage ($-9.1 \text{ kJ}\cdot\text{mol}^{-1}$, instead of -9.7 on graphite (ref. 23)) and then the molar integral enthalpy of lateral interactions (i) during the build up of the first layer up to point A ($-0.7 \text{ kJ}\cdot\text{mol}^{-1}$, instead of -1.9 on graphite) and (ii) during the phase transition, from A to B ($-1.5 \text{ kJ}\cdot\text{mol}^{-1}$, instead of -1.4 on graphite).

Peak B_1 in Fig. 1 is likely to correspond to a similar phase change of the monolayer of Ar adsorbed on ZnO.

ENERGETICAL ASPECTS OF ADSORPTION IN MICROPORES

The enhancement of the enthalpy of adsorption in micropores of molecular size still lends itself to a comparative study of N_2 and Ar adsorption since both molecules must experience this enhanced interaction, due to the overlap of the adsorption field from opposite walls of the pore. The state of affairs was well summarized by Gregg and Sing (ref. 24). Since it appears (specially from the calculations made by Everett and Powl in the case of cylindrical pores (ref. 25)) that the size of the pore must not exceed c.a. 2.5 molecular diameters to produce that enhancement, one sees that it must be studied either in zeolites (but usually with the extra influence of the cation) or in highly microporous adsorbents such as activated carbons. One then checks that the increase in differential enthalpy of adsorption is similar for N_2 and Ar. For instance, for both adsorptives, the value for zero coverage may increase from c.a. $10 \text{ kJ}\cdot\text{mol}^{-1}$ (on a flat graphite surface) to c.a. $20 \text{ kJ}\cdot\text{mol}^{-1}$ (on a microporous charcoal cloth of c.a. $880 \text{ m}^2\text{g}^{-1}$ equivalent BET surface area) (ref. 26).

Fig. 3 gives such enthalpy curves obtained with N_2 and Ar on a microporous saccharose charcoal prepared at the laboratory scale (ref. 27), with an equivalent nitrogen BET surface

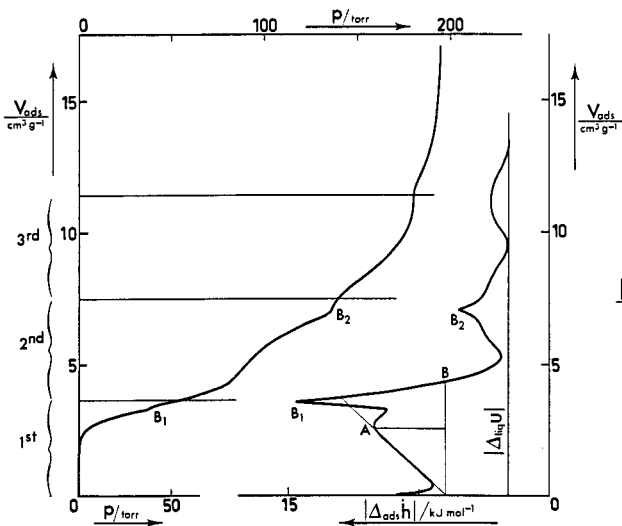


Fig. 2. High resolution adsorption isotherm (left) and differential enthalpy of adsorption (right) for the argon/boron nitride system at 77 K.

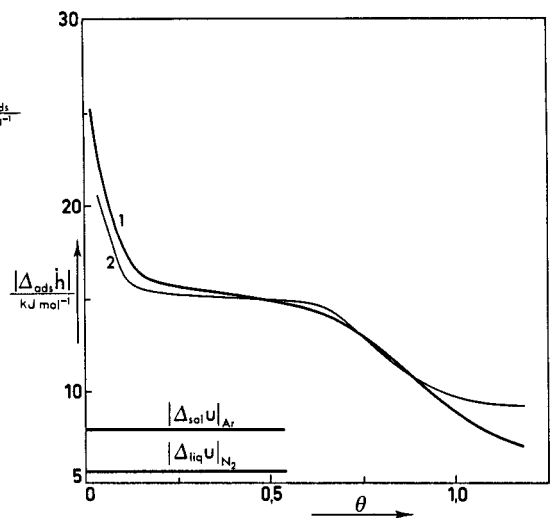


Fig. 3. Differential enthalpy of adsorption of nitrogen (curve 1) and argon (curve 2) on a microporous saccharose charcoal.

area of only $180 \text{ m}^2\text{g}^{-1}$. One may notice that both curves are very similar in shape and in values and that the high value of $25 \text{ kJ}\cdot\text{mol}^{-1}$ is reached for N_2 at the beginning of adsorption, showing, if necessary, that the fine size of the micropores is not necessarily linked with a high specific adsorption capacity. Moreover, a break is seen in both curves at a coverage (or degree of filling of the micropores) of c.a. 0.15. We noticed a similar break for other carbons : for instance, at c.a. 0.25 for the commercial activated carbon Chemviron F-400, used for potable water purification and having now an equivalent nitrogen BET surface area of c.a. $1000 \text{ m}^2\text{g}^{-1}$. The question is raised whether to attribute this break to a bimodal distribution of the micropore size or to a sharp transition from a "primary filling mechanism", involving a direct interaction of the adsorbate with the walls, to a "secondary filling mechanism" taking place in wider micropores (ref. 24) and which may still enter the scope of the volume filling of micropores early advocated by Dubinin (ref. 28).

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