

ADSORPTION OF BENZENE ON EXFOLIATED GRAPHITE BETWEEN -70°C AND -5°C

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General outlook of the isotherms.

A network of adsorption isotherms of benzene on exfoliated graphite has been determined between -70°C and -5°C by mean of a classical volumetric apparatus equipped with a McLeod gauge.

Down to the lowest studied temperature - i.e. well under the expected two dimensional critical temperature estimated from the three dimensional one - the isotherms still do not exhibit any change of curvature at low temperature and degree of covering (Fig. 1)

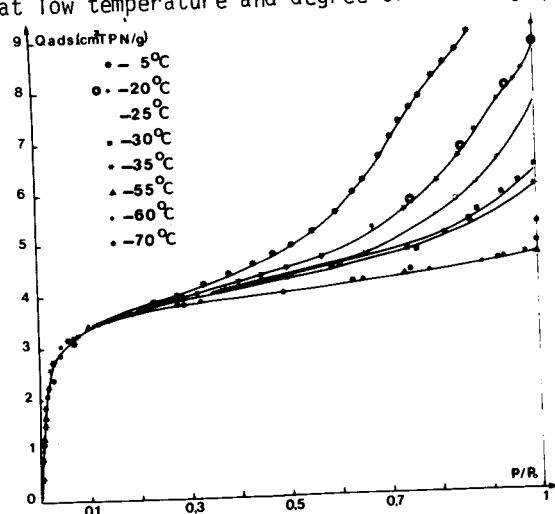


Fig. 1 : Adsorption isotherms of benzene on exfoliated graphite (● desorption at -20°C)

We confirm a quite unusual characteristic of these isotherms which intersect in the vicinity of the point B (1-2). Beyond the point B and at constant relative pressure the adsorbed amount increases with temperature.

Above -35°C , the formation of a second layer can be distinguished.

Isosteric heats and differential entropies.

In the studied temperature range neither the isotherm nor the $\log P$ vs $1/T$ plot determined from the benzene sublimation equilibrium can be represented by a single straight line. As a first approximation they can be each represented by two sets of straight lines intersecting at about -35°C , -40°C . Thus they define two temperature ranges we will call further on the low and high temperature range.

The isosteric heat and differential entropies derived from the slopes and the intercepts on the ordinate axis for $1/T = 0$ of the straight line portions of the isosteres are plotted on figures 2 and 3 versus the adsorbed amount.

In the low temperature range (Fig. 2), the isosteric heat decreases linearly with the adsorbed amount whereas the differential entropy increases from zero covering to adsorbed amounts corresponding to rela-

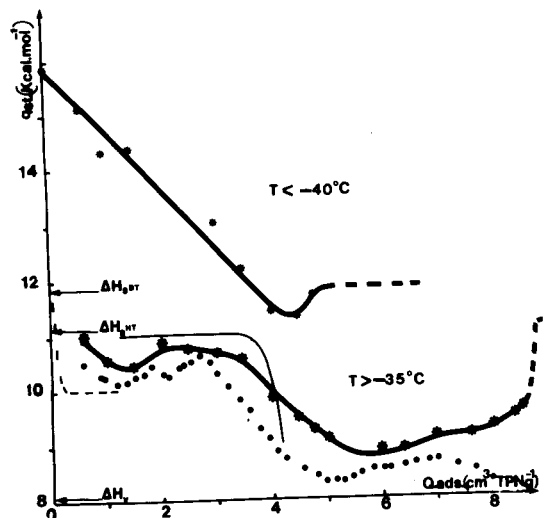


Figure 2 : Variation of the isosteric heat.
* low temperature range ($T < -40^{\circ}\text{C}$)
* high temperature range ($T > -35^{\circ}\text{C}$)
— PIERCE and EWING (2) ($-10^{\circ}\text{C} < T < -20^{\circ}\text{C}$)
● PIEROTTI and SMALLWOOD (3) ($0^{\circ}\text{C} < T < 50^{\circ}\text{C}$)
--- DOLLIMORE, HEAL and MARTIN (4) ($80^{\circ}\text{C} < T < 97^{\circ}\text{C}$)
 ΔH_s BT enthalpy of sublimation (in the low temperature range).
 ΔH_s HT enthalpy of sublimation (in the high temperature range).

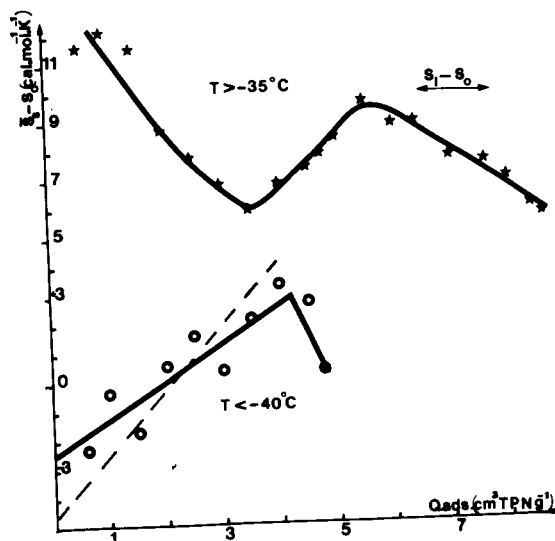


Fig. 3 : Variation of the differential entropy
* high temperature range
* low temperature range
--- estimation of the variation of the thermic entropy
 $S_L - S_0$ molar entropy of fusion of benzene at -50°C

tive pressures close to unity (Fig. 3).

In the high temperature range, the isosteric heat is more or less constant up to point B then, decreases and increases again during the formation of the second layer. This is quite consistent with the results of PIERCE and EWING (2) and those PIEROTTI and SMALLWOOD (3) and DOLLIMORE, HEAL and MARTIN (4) obtained above the three dimensional triple point temperature (Fig. 2). The variation of the differential entropy with covering can be rather straightforwardly interpreted as a first decrease caused by a compression of the first layer, a further increase caused by the beginning of the formation a second layer and a last decrease caused by the compression during the completion of the second layer (Fig. 3).

Determination of benzene cross-section and degree of covering.

Since the early work of KISELEV (5) most of the previous authors (3, 4) have supposed the benzene molecule cross-section to be equal to $40 \text{ \AA}^2$. This value is consistent with a hexagonal close-packed arrangement of molecules laying flat on the graphite surface. Monolayer capacity had been computed either on the assumption of monolayer completion at the point B (1) or by mean of BET equation (3). We found that BET isotherm linearization gives a rather poor fitting and capacity values 85 to 90 % smaller than the point B.

Systematic graphite surface controls have been performed by krypton adsorption at liquid nitrogen temperature. From the value of the adsorbed amount at the point B and on the assumption that krypton atom cross-section is equal to $14,3 \text{ \AA}^2$ (6), benzene cross-section can be computed using the following equation:

$$\sigma_{\text{C}_6\text{H}_6} = \frac{q_m(\text{Kr})}{q_{\text{C}_6\text{H}_6}} \sigma_{\text{Kr}}$$

$$q_m(\text{Kr}) = 9,5 \text{ cm}^3 \text{ NTP g}^{-1} \text{ (point B of Kr isotherm)}$$

$$\sigma_{\text{Kr}} = 14,3 \text{ \AA}^2$$

$$q_{\text{C}_6\text{H}_6} = \text{adsorbed amount of benzene (cm}^3 \text{ NTP g}^{-1}\text{)}$$

On Table I the cross-section computed from various points of the isotherms are compared with the cross-section of the benzene molecule in the low-Miller-index surfaces of the three dimensional benzene crystal at -50°C (7).

The BET capacity yields a cross-section consistent with an arrangement of close packed molecules parallel to the surface and the point B yields a somewhat smaller value. However it is to be emphasized that the values derived from adsorbed amounts in the vicinity of unit relative pressure in the low temperature range are much smaller and very near to the cross-section in the benzene crystal planes of high density (in this temperature range the shape of isotherm, the variation of isosteric heat and differential entropy give strong evidences that there is a single adsorbed layer up to the saturation vapor pressure).

The high density of molecules in (010) (100) (111) planes is accounted by the fact that the molecules are tilted with respect to one another in order that every molecule presents a maximum interaction with its neighbours.

TABLE I

Basis of cross-section determination	($\text{\AA}$)	$q(\text{cm}^3 \text{ NTP g}^{-1})$
BET equation	41,2	3,3
Point B	38,8	3,5
$q_{\text{C}_6\text{H}_6}$ near $P/P_0 = 1$		
- at -70°C	30,2	4,5
- at -40°C	27,2	5,0
(001) benzene crystal plane	35,7	
(010) -	25,8	
(100) -	33,5	
(111) -	27,6	

Since the π - π mutual interaction of benzene molecules is very similar to benzene-graphite interaction (this is attested by a heat of adsorption close to the heat of sublimation) - a possible tilting of adsorbed molecules at high coverage due to lateral interaction can well be considered that would explain the small cross-section calculated.

Discussion.

The experimental values of differential entropy has been compared with theoretically computed values based upon the different modes of molecular motion available to the adsorbed molecule.

In the low temperature range, the experimental values are in accord with a model of localized molecules adsorbed flat on the graphite surface at low coverage. Increasing coverage induces a progressive tilting of the molecules caused by lateral interactions and allows the progressive release of two degrees of rotational freedom. Hence the monolayer capacity will increase with temperature.

In the high temperature range the adsorbed phase seems to be in the same state described by earlier workers (8, 3, 4) for temperature ranges above the 3D. melting point (i.e. mobile layer with two degrees of rotational freedom ruled by a 2D. VOLMER equation of state).

These results implies that it exists a second order phase transition in the first layer about -40°C , quite insensitive to the pressure, between a localized and a mobile hypercritical phase.

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