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Adsorption of the first layer of argon on graphite (*)

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Résumé. — Nous avons déterminé des isothermes d'adsorption d'argon sur le graphite entre 55 et 62 K. Nous proposons une interprétation de nos résultats.

Abstract. — I have determined a set of adsorption isotherms for argon on graphite from 55 to 62 K. An interpretation of the results is proposed.

Argon on graphite isotherms have been determined by volumetry with a modified MacLeod gauge previously described by Larher [1]. The cooling bath is solid nitrogen obtained by pumping. The adsorption cell, enclosed in an aluminum block, is regulated to within 0.01 K. Using a nitrogen vapour pressure bulb and an oil manometer the temperature is known with a precision of 0.01 K. Pressures are corrected for thermal transpiration [2] and mercury drag effect [3]. The graphite sample is an uncompressed grafoil from Union Carbide which was previously heated in vacuum at 400 °C. Its specific surface area is accurately determined from a nitrogen isotherm at 62 K (see Fig. 1) as 26.5 m²/g (the end of the rise of isotherm 5 corresponds to the density of a registered \( \sqrt{3} \times \sqrt{3} \) solid [4, 5]). From the isotherms of figure 1 the critical temperature of the gas-dense phase transition was found to be \( T_c = 58 \pm 1 \) K. An accompanying isostere was made at 1.6 μmole (see Fig. 2). This data follows the linear fit

\[
\log_{10} P(\text{torr}) = -\frac{607.5}{T} + 7.14
\]

with standard deviations

\[
(607.5) = 2.4 \quad \text{and} \quad (7.14) = 0.04
\]

The relations between the vapour pressure of the transition \( P^{(1)} \) and that of solid argon \( P^{(s)} \) at the same temperature are [6] :

\[
\text{Fig. 1.} \quad \text{Adsorption isotherms for argon: 1) 54.61 K; 2) 55.75 K; 3) 59.53 K; 4) 62.41 K, nitrogen; 5) 62.11 K (uncorrected pressures).}
\]

\[
\text{Fig. 2.} \quad \text{Isosteres at 1.6 μmole and 4.3 μmole. The highest pressure point is from Larher's work [4].}
\]
From these relations the internal energy and entropy were deduced to be:

\[
\log \frac{p^{(x)}}{p^{(1)}} = \frac{u^{(x)} - u^{(1)}}{RT} + \frac{s^{(1)} - s^{(x)}}{R}
\]

and

\[
d \log \frac{p^{(x)}}{p^{(1)}} = \frac{u^{(x)} - u^{(1)}}{R}.
\]

From these relations the internal energy and entropy were deduced to be:

\[
u^{(x)} - u^{(1)} = 3.565 \pm 46 \text{ J.mol}^{-1},
\]

\[
s^{(1)} - s^{(x)} = 11.7 \pm 0.8 \text{ J.mol}^{-1} \text{K}^{-1}
\]

respectively.

The nature of the dense phase formed during this first-order transition can be inferred in two ways. First, the end of the vertical rise of the 55.75 K isotherm corresponds to the density of the registered solid nitrogen when compared with the nitrogen isotherm of figure 1. Second, the entropy \(s^{(1)} - s^{(x)}\) of the transition is compared in table I and figure 3 to that of numerous registered phases of simple gases on lamellar halides. It has been shown [7] that the entropy of these transitions is sensitive to the dimensional incompatibility between the adsorbate and the adsorbent. In the particular case of a registered phase the dimensional incompatibility is the dilatation of the film from its natural 3D spacing. My result fits well with the curve of figure 3 for a solid argon layer diluted by 12% which corresponds to a \(\sqrt[3]{3} \times \sqrt[3]{3} \text{ R} \ 30^\circ\) registered phase. It is also shown that the entropy of the known \(\sqrt[3]{3} \times \sqrt[3]{3} \text{ R} \ 30^\circ\) phase of krypton on graphite [8] is consistent with this curve and that the data of Thomy and Duval [9] for xenon on graphite can be interpreted as a \(2 \times 2\) registered phase instead of the liquid suggested by these authors. Diffraction techniques [10, 11] do not show any well ordered and registered solid argon monolayer. At least, neutrons [11] show at 55 K and a density of 0.062 \(\text{A}^{-2}\) an argon-argon spacing close to the registered spacing. A compression of the solid out of registry is seen on the 55.75 K isotherm above 3.45 \(\text{mole}\). A new break occurs at 4.3 \(\text{mole}\). At this point the density of the film corresponds to a triangular lattice with argon atoms 3.8 \(\text{Å}\) apart. This regime appears to be very different on the 59.53 K and 62.41 K isotherms.

An ill-defined fluid-solid transition, already observed at higher temperatures by Grillot et al. [12] and Larher [13], takes place followed by a compression up to 4.3 \(\text{mole}\). The vapour pressure of the break points at 4.3 \(\text{mole}\) is plotted on figure 2. They lie on a straight line which crosses the gas to registered phase isostere at about 50 K. This suggests the existence of a triple point and below 50 K a further gas to unregistered solid phase transition (Shaw and Fain [14] have shown that argon condenses at 51 \(\pm 1\) K to an out of registry solid).

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Table I. — Entropies and incompatibilities \(i\) of registered phases of rare gases on graphite \((i = \frac{a - d}{d})\); \(a\) stands for the distance between two adsorption sites and \(d\) for the natural 3D spacing of the adsorbate.

<table>
<thead>
<tr>
<th>Gas</th>
<th>(s^{(1)} - s^{(x)})</th>
<th>Hypothetic phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>argon</td>
<td>11.7</td>
<td>(\sqrt[3]{3} \times \sqrt[3]{3}) R 30 (i = 12)</td>
</tr>
<tr>
<td>krypton</td>
<td>1.1</td>
<td>(\sqrt[3]{3} \times \sqrt[3]{3}) R 30 (i = 4.6)</td>
</tr>
<tr>
<td>xenon</td>
<td>9.2</td>
<td>(2 \times 2) (i = 11.7)</td>
</tr>
</tbody>
</table>

![Fig. 3. — Entropy vs. incompatibility for argon (A), krypton (K), xenon (X), methane (M) on lamellar halides and rare gases on graphite (O).](image)

References