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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 aluminium 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

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

with standard deviations

(607.5) = 2.4 and (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]:

\[
\log_{10} \frac{p^{(1)}}{p^{(s)}} = - \frac{607.5}{T} + 7.14
\]
From these relations the internal energy and entropy were deduced to be:

$$u^{(\infty)} - u^{(1)} = 3.565 \pm 46 \text{J.mol}^{-1},$$

$$s^{(1)} - s^{(\infty)} = 11.7 \pm 0.8 \text{J.mol}^{-1}.K^{-1}$$

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 $s^{(1)} - s^{(\infty)}$ 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 $3 \sqrt[3]{3} R 30^\circ$ registered phase. It is also shown that the entropy of the known $3 \sqrt[3]{3} \times 3 \sqrt[3]{3} R 30^\circ$ 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 Å⁻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 Å⁻¹ mole. A new break occurs at 4.3 Å⁻¹ mole. At this point the density of the film corresponds to a triangular lattice with argon atoms 3.8 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 Grillet et al. [12] and Larher [13], takes place followed by a compression up to 4.3 Å⁻¹ mole. The vapour pressure of the break points at 4.3 Å⁻¹ 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 ± 1 K to an out of registry solid).

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References


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

![Table I. — Entropies and incompatibilities of registered phases of rare gases on graphite](image_url)