

Heats of adsorption of methane multilayers on graphite

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Isosteric heats of adsorption of CH₄ on exfoliated graphite (Grafoil) have been measured calorimetrically at 69.5, 77, 84.5, and 92.5 K up to surface coverages of the equivalent of 3.5 layers. At the lowest two temperatures, q_{st} varies rather little with the amount adsorbed beyond a monolayer. In the same region of adsorption, q_{st} at the highest two temperatures changes by as much as 10% in an oscillatory manner. A qualitative analysis of the results suggests that they are consistent with a transition (roughening?) occurring in the methane multilayers in the vicinity of $T=80$ K. From isotherm and heat-capacity measurements on the same system, Hamilton and Goodstein [Phys. Rev. B 28, 3838 (1983)] have deduced that critical points in the multilayers occur at approximately 78 K.

I. INTRODUCTION

The phase diagram of methane adsorbed on graphite has been characterized moderately well in the region of one monolayer or less adsorbed through isotherm,^{1,2} neutron diffraction³ and scattering,^{2,4} NMR,⁵ and heat-capacity⁶ measurements. Much less attention has been paid to adsorption in the multilayer region until recently, except to demonstrate that the multilayers are formed in a stepwise fashion.² In a recent paper, Hamilton and Goodstein⁷ made a thorough thermodynamic study of methane multilayers adsorbed on graphite, based on measurements of isotherms and heat capacities, and were guided by a comprehensive theoretical investigation of physisorbed multilayers.⁸ The work described in this paper complements the study by Hamilton and Goodstein. It provides rather accurate information about the variation of the isosteric heat of adsorption with surface coverage through the temperature region where Hamilton and Goodstein found changes in the behavior of multilayers which they ascribed to a layer-dependent critical transition that would be expected⁸ to merge with a roughening transition in bulk solid methane. In the course of the measurements of q_{st} , equilibrium vapor pressures and a few heat capacities were also determined. The combined results are used to compute differential molar entropies which are often useful for making deductions about the configurations of the adsorbed layers.

II. EXPERIMENTAL

The heats of adsorption were measured with an adiabatic calorimeter which has been fully described elsewhere.⁹ Briefly, the technique consists of measuring small changes in temperature and pressure which result from adsorbing increments of gas in the calorimeter over a range of ± 0.5 K from a chosen temperature. The initial quantity obtained is a change in the integral heat of adsorption Q :

$$\Delta Q = [C_p(\text{cal}) + C_a(\text{ads}) + C_p(\text{g})]\Delta T - V_{\text{cal}}\Delta P, \quad (1)$$

where C denotes the heat capacity: $C_p(\text{cal})$ of the

calorimeter plus adsorbent, $C_a(\text{ads})$ of the adsorbed film, and $C_p(\text{g})$ of the vapor in the calorimeter. The quantity $V_{\text{cal}}\Delta P$ is the heat of compression of the vapor in the free volume of the calorimeter vessel. The isosteric heat of adsorption, q_{st} , is simply $\Delta Q/\Delta n_a$, where Δn_a is the number of moles adsorbed in the increment. An assessment of the results of previous measurements^{9,10} with the calorimeter system, corrected to a chosen temperature, indicates that q_{st} is obtained with an accuracy better than $\pm 1\%$. The precision, which is more pertinent for the results reported here, is better than $\pm 0.4\%$.

The methane gas was obtained from a commercial source (Matheson, Research Purity, 99.99%) and was used without further purification. The monolayer capacity of the Grafoil for methane, as estimated by the Brunauer-Emmett-Teller method, was found to be 2.9×10^{-3} mol (cf. 3.0×10^{-3} mol for nitrogen adsorbed on the same Grafoil specimen).⁹ This estimate is adequate for defining the extent of the multilayer adsorption. If it were required, a more accurate value could be computed from the registered monolayer capacity for nitrogen⁹ and the relative lattice spacings of nitrogen and methane.¹¹

III. RESULTS

The isosteric heats of adsorption, q_{st} , are illustrated in Fig. 1. They were determined over the complete range of surface coverage ($0 < \Theta < 3\frac{1}{2}$ monolayers) at only one temperature—84.5 K. Integral heats of adsorption, Q , were obtained at $T=92.5$ K and $T=84.5$ K but they are not recorded here because they are not used in subsequent thermodynamic analyses.

Several features displayed by the results shown in Fig. 1(a) can be readily understood. The initial larger values of q_{st} at the lowest surface coverages undoubtedly arise from the presence of some higher-energy adsorption sites on the Grafoil surface. The same effect was observed in the earlier studies of nitrogen⁹ and xenon¹⁰ adsorption. An extrapolation to zero coverage that neglects the surface heterogeneity yields

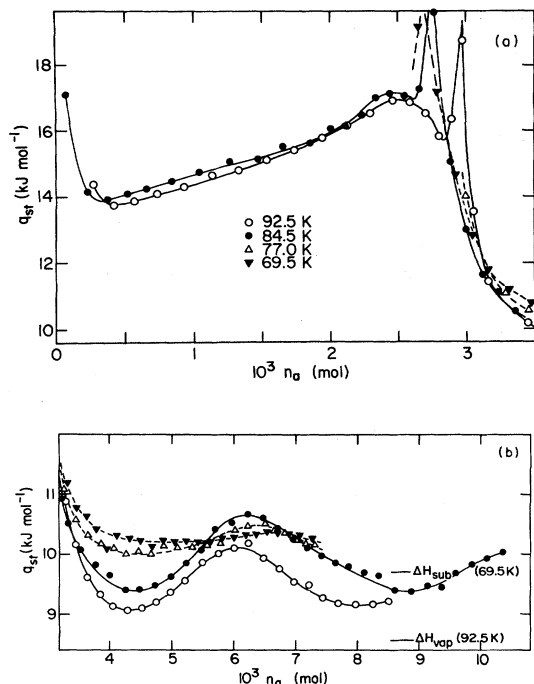


FIG. 1. (a) Measured isosteric heats of adsorption (q_{st}) as a function of the amount adsorbed for $\Theta < 1.1$. (b) Measured isosteric heats of adsorption (q_{st}) as a function of the amount adsorbed for $\Theta > 1.0$. Note different scales for (a) and (b).

$$q_{st}(0) = 13.7 \pm 0.1 \text{ kJ mol}^{-1} \text{ at } T = 84.5 \text{ K}$$

and

$$q_{st}(0) = 13.4 \pm 0.1 \text{ kJ mol}^{-1} \text{ at } T = 92.5 \text{ K}.$$

These values agree well with the heat of adsorption at low surface coverage ($\Theta \sim 0.1$) which has been computed¹ from isotherm data in the range 77.3–90.1 K: 13.8 kJ mol⁻¹. For graphitized carbon black, the heat of adsorption of light methane at zero coverage and $T = 235$ K has been estimated¹² to be 12.7 kJ mol⁻¹.

The increase in q_{st} in the range $0 < n_a < 2.5 \times 10^{-3}$ mol is brought about by interactions between the adsorbed methane molecules. The magnitude found here ($\Delta q_{st} = 3.4 \text{ kJ mol}^{-1}$) is exactly the same as that quoted¹³ as the average for Δq_{st} at $T = 128$ K for several sets of adsorption experiments on graphitized carbon black. Without some further detailed investigation, little can be said about the apparent disappearance of the systematic displacement of the two sets of results for q_{st} at about $n_a \approx 2 \times 10^{-3}$ mol. It is possible that the measurements at $T = 84.5$ K are sensing the two-phase liquid-gas region of the phase diagram (see Fig. 6 of Ref. 7).

The peaks in q_{st} displayed at the higher surface coverages in Fig. 1(a) are the consequence of a region of coexistence of liquid- and solid-surface phases. They are somewhat broader than the existing phase diagram (Fig. 6 of Ref. 7) would suggest. For $T = 92.5$ K, the phase diagram places the two-phase region at a surface coverage of 0.9 of a monolayer. This implies a monolayer coverage of 3.3×10^{-3} mol for methane on the calorimetric specimen of Grafoil.

The unusual results which have been found are displayed in Fig. 1(b)—the large-amplitude oscillations of q_{st} as a function of surface coverage at $T = 84.5$ and 92.5 K. The variations at the other two temperatures are considerably less. When these results became known, Hamilton and Goodstein¹⁴ derived heats of adsorption from their extensive isotherm data,¹⁵ oscillations of q_{st} of similar magnitude were found for $T > 78$ K. At this stage, it seems only possible to propose a qualitative account of the observations. Before that is done, the behavior of some other properties of the adsorbed multilayers will be discussed briefly.

The chemical potential of the adsorbed phase, which is equal to that of the vapor with which it is in equilibrium, was computed from the measured pressures and temperatures with an allowance being made for vapor imperfection and for a rotational contribution:

$$\begin{aligned} \mu_a &= \mu(T, P) \\ &= kT \ln \left[\frac{P}{kT} \left(\frac{2\pi\hbar^2}{mk} \right)^{3/2} \right] + B(T)P + \mu_{rot}. \end{aligned} \quad (2)$$

Here, $B(T)$ is the second virial coefficient of methane. The results are plotted in Fig. 2. The curves are very similar in shape and magnitude to those computed by Hamilton and Goodstein⁷ (see Fig. 5 of their paper) but they are less sharp. This is not surprising since it is known^{16,17} that stepwise multilayer adsorption and phase transitions are not so well marked on graphite substrates which have been compressed, e.g., on Grafoil, as was used here. Hamilton and Goodstein used an expanded form of exfoliated graphite, Grafoam, for their experiments. Results for nitrogen adsorption on Grafoil⁹ displayed a more

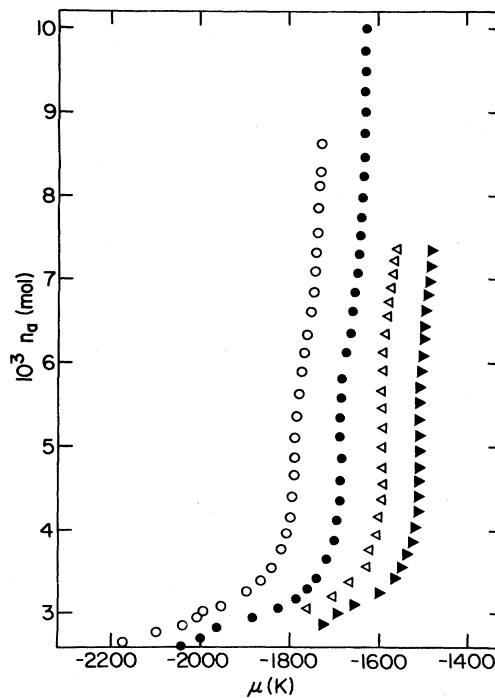


FIG. 2. Chemical potential of adsorbed methane as a function of the amount adsorbed. Symbols are the same as in Fig. 1.

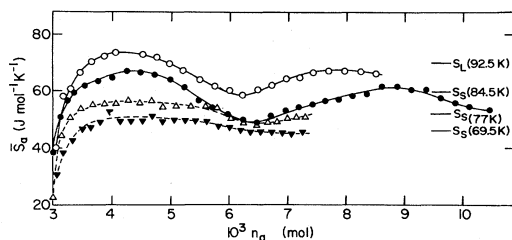


FIG. 3. Differential molar entropy \bar{S}_a as a function of the amount adsorbed. Symbols are the same as in Fig. 1.

rounded transition to a commensurate solid phase than is observed for uncompressed graphite.

The differential molar entropies of the adsorbed methane are plotted in Fig. 3. They were computed from

$$\bar{S}_a = S_g - \frac{q_{st}}{T} - \alpha P, \quad (3)$$

where S_g is the molar entropy of the equilibrium vapor at P and T , and α is a factor to allow for gas imperfection. It can often be obtained with sufficient accuracy from a modified Berthelot equation of state¹⁸ which contains critical parameters of the gas or vapor:

$$\alpha = \frac{27}{32} \frac{RT_c^3}{P_c T^3}. \quad (4)$$

Changes in \bar{S}_a mirror the changes in q_{st} with the amount adsorbed, as would be expected from the relationship between the two quantities [Eq. (3)].

Heat capacities of the adsorbed phase were needed for the determination of the heats of adsorption [Eq. (1)] and some direct measurements were made for that reason. The results are displayed in Fig. 4. The scatter is large because the heat capacity of the adsorbed phase was 4% of the total at most, but there is an indication that C_a goes through a broad maximum in the vicinity of $T=85$ K. There is also some indication of a concentration dependence at the higher temperatures as suggested by the dashed curves.

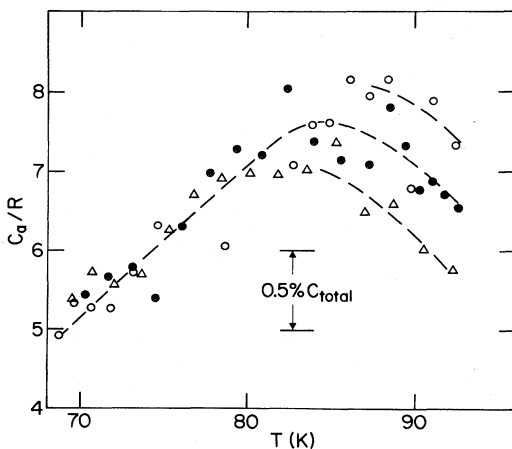


FIG. 4. Heat capacity of adsorbed methane as a function of temperature: \circ , $\Theta=2.4$; \bullet , $\Theta=2.0$; \triangle , $\Theta=1.6$.

The magnitude of the measured heat capacities are consistent with those found by Hamilton and Goodstein.⁷ On the basis of their results, one would not expect to observe a sharp peak in the heat capacity for $\Theta \leq 2.4$ to indicate melting of the adsorbed film in the vicinity of $T=90$ K.

IV. DISCUSSION

In this study, the adsorption of the methane was not followed to the saturation pressure to determine its class:^{19,20} class I (complete wetting), class II (incomplete wetting), or class III (nonwetting). It is presumed that the adsorption is class I and that the wetting transition, which has not been definitely pinpointed for the methane/graphite system, would occur well below the temperature of these experiments. The isotherm data, when plotted in terms of relative pressures, show (not illustrated) a temperature dependence similar to that reported by Prenzlou and Halsey²¹ for krypton adsorbed on graphitized carbon black. The isotherm steps become more rounded with increasing temperature. The same aspect is apparent in large-scale plots of the chemical potential for the data obtained here and by Hamilton and Goodstein.⁷ Thus, from the adsorption data alone, it is not at all evident that the behavior of the adsorbed methane multilayers changes so markedly in the region of $T=80$ K. Nevertheless, the differential enthalpy (q_{st}) and differential entropy (\bar{S}_a) show marked changes in their coverage dependence between 77 and 84.5 K. At all of the temperatures studied, \bar{S}_a shows a minimum at about $\Theta=2$. This might be expected for layer-type adsorption because the configurational contribution to the entropy would be a minimum here. In addition, in the building up of a second layer, one might expect to see an increase in the heat of adsorption due to the increase in the number of adsorbed neighbors—as is observed for the first layer. That is consistent with the change in q_{st} for $4 \times 10^{-3} < n_a < 6.5 \times 10^{-3}$ mol, but why is the change so much more muted at the lowest temperature? A possibility is that a two-phase region forms for $T < 80$ K through a critical transition that is essentially independent of surface coverage, as suggested by Hamilton and Goodstein.⁷ Adsorption into a two-phase system would mute variations in the heat of adsorption.

Oscillations in the isosteric heat of the adsorption with surface coverage have been reported for two other systems: argon adsorbed on bare and xenon-covered graphitized carbon black,²¹ and ammonia on graphitized carbon black.²² In the latter case, the transition from class-II to class-I adsorption is probably involved. A Monte Carlo study of physical adsorption²³ applied to the former case displays oscillations in q_{st} with surface coverage which are damped with increasing temperature. This study of the methane/graphite system has not been made over a sufficiently wide temperature region to test that feature of the statistical calculations.

It has been shown by Sullivan²⁴ that there can be a delicate balance between thermal energy and intermolecular and gas-substrate energies such that modest changes in temperature can produce, for example, transitions between

different classes of adsorption. It is an extension of Sullivan's ideas by Pandit *et al.*⁸ which guided the investigation of the methane/graphite system by Hamilton and Goodstein.⁷ Their experimental results and ours may perhaps encourage theoretical calculations to delineate the transition that clearly is occurring in the methane multilayers in the region of $T = 80$ K.

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