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Two-dimensional phase diagram of neon adsorbed on exfoliated graphite. Heat-capacity measurements

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Heat-capacity measurements of neon adsorbed on bare Grafoil for coverages between 0.100 and 0.900 of a monolayer were made as a function of temperature in the range of 6.0 to 20.0 K using the quasiadiabatic method. From the data a two-dimensional phase diagram was constructed which indicates a triple-point temperature of 13.57 K and a critical-point temperature of about 15.8 K. Whenever possible our results are compared with the data obtained by other authors.

I. INTRODUCTION

Heat-capacity measurements of adsorbed films on uniform substrates have been used to identify phase transitions as a function of coverage and temperature. Recently heat-capacity measurements have been made for adsorbed gases on exfoliated graphite, Grafoil (made by Union Carbide), or on Grafoil preplated with another gas.

Adsorption isotherms and scattering measurements of Xe, CH_4, and O_2 (Ref. 1) show evidence of a two-dimensional solid behavior at low temperatures and a coexistence region between the expected triple and critical points. Heat-capacity measurements of Ne,[2] O_2,[3] N_2,[4] and Kr (Ref. 5) on Grafoil show the existence of a peak in the specific heat which appears to be the triple point, but a confirmation of this depends on identifying the liquid and vapor phases and their coexistence region.

Steele and Karl[6] report peaks in the specific-heat measurements of Ne, Ar, and Kr adsorbed on graphitized carbon black. For the Ne, they found the peak at 16.1 K for a coverage of 0.5 monolayer. Antoniou[7] measured the heat capacity of Ne adsorbed on graphitized carbon and found peaks for the 0.6 and 1.0 coverages at about 12 and 15 K, respectively. Thomy *et al.*[8] reported a first-order transition of neon adsorbed on Grafoil from an isotherm at 20.4 K for a coverage around 0.9. Huff and Dash[2] made the first set of specific-heat measurements of Ne adsorbed on Grafoil, for submonolayer coverages in the temperature range of 2 – 20 K. The main features of the specific-heat signature are large sharp peaks at constant temperature as a function of coverage, and a second wide and small peak. The authors interpreted the first anomaly as being the triple-point transition. Probably due to poor resolution they were not able to use the second anomaly to construct a more complete phase diagram.

The heat-capacity measurements presented in this paper confirm the anomalies obtained by Huff and Dash. We were able to obtain a more complete phase diagram due to an annealing procedure which improved the resolution of the heat-capacity signature, especially at temperatures above the one where the first anomaly appears, and consequently obtain a better definition of the second peak. This peak moves up in temperature as the coverage increases to 0.430 coverage and then starts to move down in temperature to the 0.550 coverage, after which it disappears. This is taken as evidence of the existence of a critical point.

Isotherms of the heat capacity as a function of coverage were constructed allowing us to observe a coexistence region for temperatures below the triple-point line (which was also observed by Huff and Dash). The region between the triple line and the second peak curve is expected to be a liquid-vapor coexistence region. The dispersion in the heat-capacity data does not allow us to have a clear-cut definition of this coexistence region, although the heat-capacity isotherms give evidence of its existence.

II. EXPERIMENTAL ARRANGEMENT

Heat-capacity measurements were obtained using a cryostat described in detail elsewhere[9] which had a calorimeter as shown in Fig. 1, built in such a way to have a very good thermal contact between the Grafoil and the calorimeter itself. It consists of five perforated disks which are screwed together

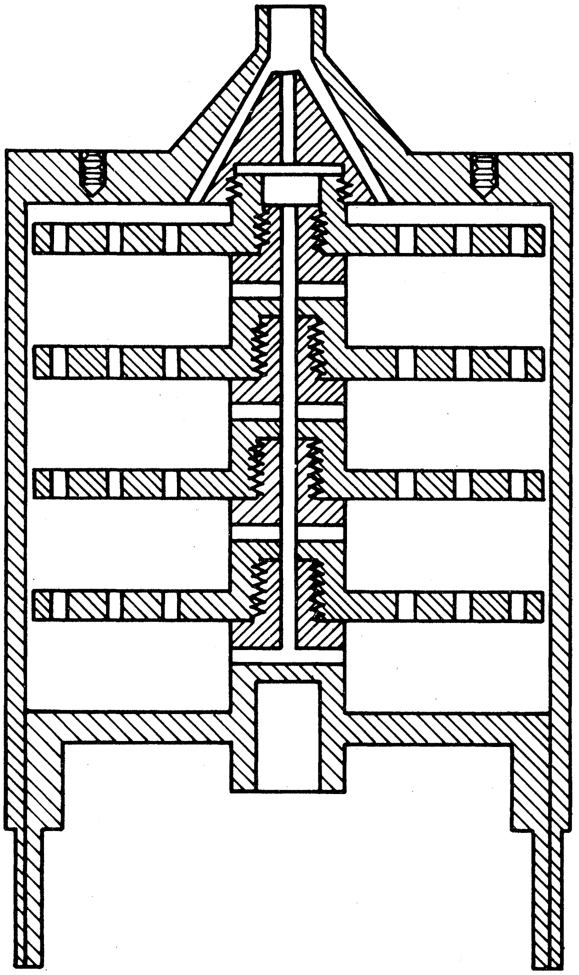

FIG. 1. Schematic diagram of calorimeter.

through central threaded bosses as shown in Fig. 1. Grafoil ribbons 5.60 mm wide, 0.125 mm thick, and long enough to completely fill the space between the boss and the calorimeter's internal wall were wound around the bosses. The disks, which in the final assembly are 5.50 mm apart, were then screwed together, gently squeezing the Grafoil, allowing a good thermal contact between it and the calorimeter, and avoiding in this way the necessity of introducing any good conducting material, as copper powder for example, which could change the Grafoil's surface characteristics. The last disk is built in such a way as to fit tight in the lower inside part of the calorimeter wall permitting a good vacuum seal with silver solder, and this was done inside an argon-atmosphere oven. The total mass of the copper was (178.02 ± 0.02) g and of the Grafoil (16.64 ± 0.02) g. Incoming gas is distributed in the calorimeter's interior through the existing holes and grooves in the disks. The gas used was neon research grade from Matheson Gas Products.

Temperatures were measured with a CR 1000 Cryocal germanium resistor (7.3 ohm at room temperature, 1200 ohm at 4 K) at the calorimeter and an Allan Bradley resistor (180 ohm at room temperature $\frac{1}{4}$ W) at the shield, both calibrated using a factory-calibrated CR 1000 germanium resistor.

The shield temperature was controlled by an Artronix regulator and the vapor pressure of the neon gas was measured with a Texas Instrument precision gauge. Heat pulses for the heat-capacity measurements were produced and measured through a bifilar Evanohm wire electric heater (1000 ohm) attached to the calorimeter with GE 7031 varnish, a power supply, a digital cronometer (both homemade), two Hewlett Packard (HP) digital voltmeters and a superconductivity Helium Electronic Corp. (SHE) ac resistance bridge. Temperature drifts and changes were monitored by a Kepp and Zonen chart strip recorder.

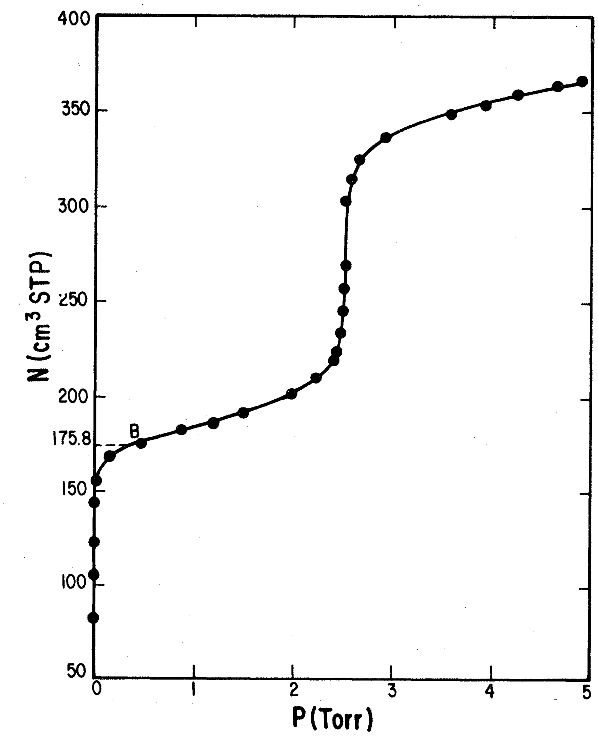

FIG. 2. Neon isotherm at 19.5 K.

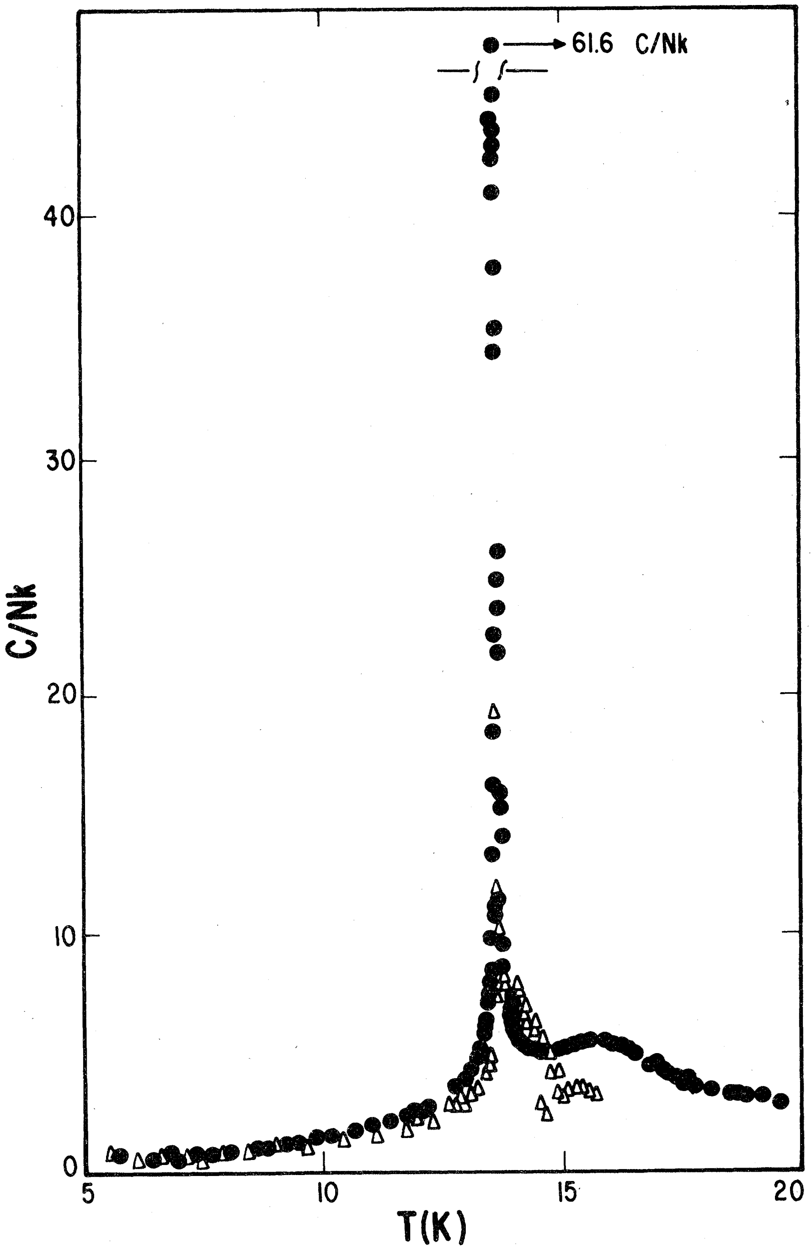

FIG. 3. Heat-capacity measurements as a function of temperature for 0.500 coverage. (Δ) before annealing and (●) after annealing.

III. NEON ISOTHERM

In order to determine the monolayer capacity, a neon isotherm at 19.5 K was obtained, and it is shown in Fig. 2. Using the point B method[10] we found a monolayer volume of 175.8 cm^3 (STP) which gives an area of 408.0 m^2 for our sample and a specific area of 24.5 m^2/g for the Grafoil which is larger than the one given by Bretz[11] and has the same value as that reported by Huff.[12] Different specific areas are obtained probably due to different cleaning treatments. The adsorbent was cleaned at 400 °C during 12 h in vacuum.

IV. HEAT-CAPACITY MEASUREMENTS

The heat-capacity measurements were made using the classical quasiadiabatic method. Heat pulses were always 50 sec long with intensities such to per-

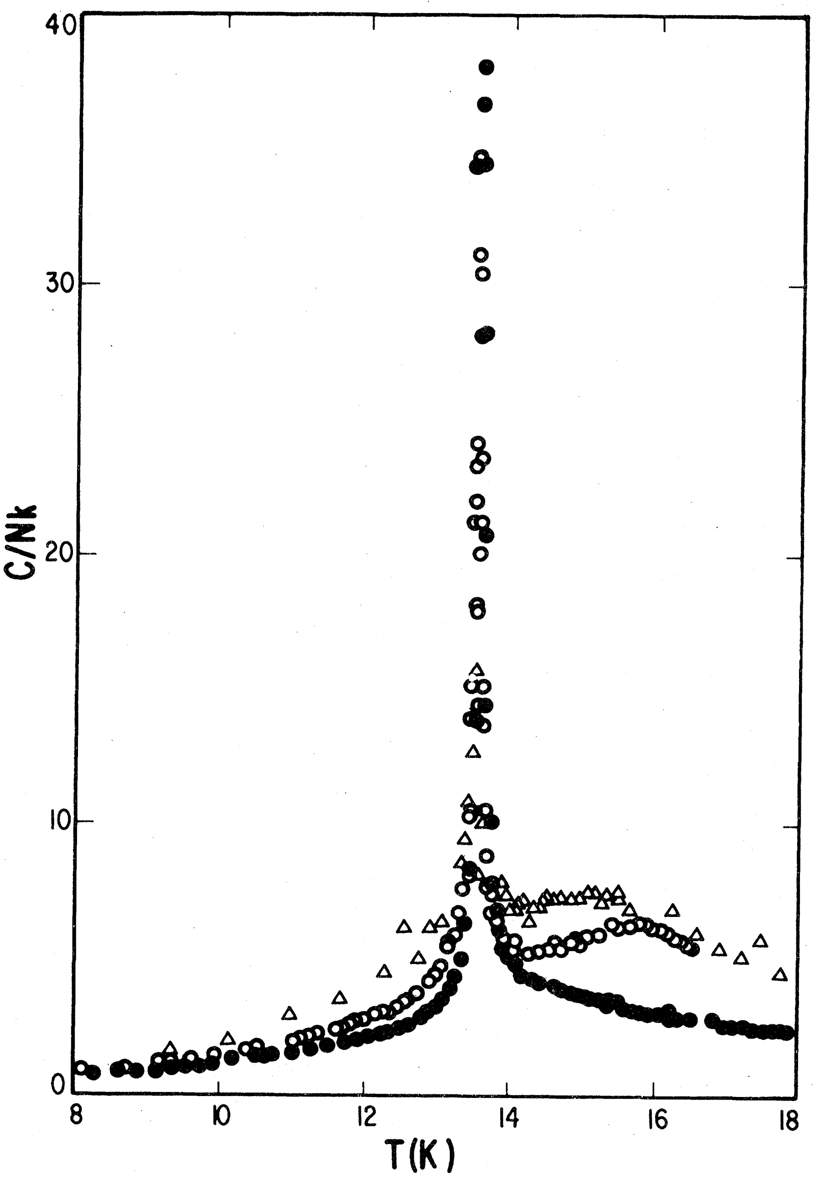

FIG. 4. Heat-capacity measurements as a function of temperature for (Δ) 0.217, (○) 0.380, and (●) 0.700 coverages.

mit temperature increments of about 1%, but for the measurements close to the anomalies 0.2% was a typical value (about 0.030 K). The internal time constant (after the heat pulse was applied) was shorter than three min and the external time constant (after changing the shield or the calorimeter temperature) was longer than a few hours in the worse situation.

A. Background

Heat-capacity measurements of the calorimeter without and with Grafoil were made, which gave us the Grafoil's heat capacity.[13] A sixth-order polynomial was adjusted to our data obtained for the calorimeter plus Grafoil and was used to subtract the background from our final measurements. An error analysis was made, by repeating these measurements, which indicated that our error was less than 0.5%. However, as the neon-film heat capacity is only about 10% of the total heat capacity measured, the final error in the film heat capacity was less than 5%.

B. Adsorbed neon film

On making measurements of the 0.500 monolayer coverage it was noticed that an unusual scatter

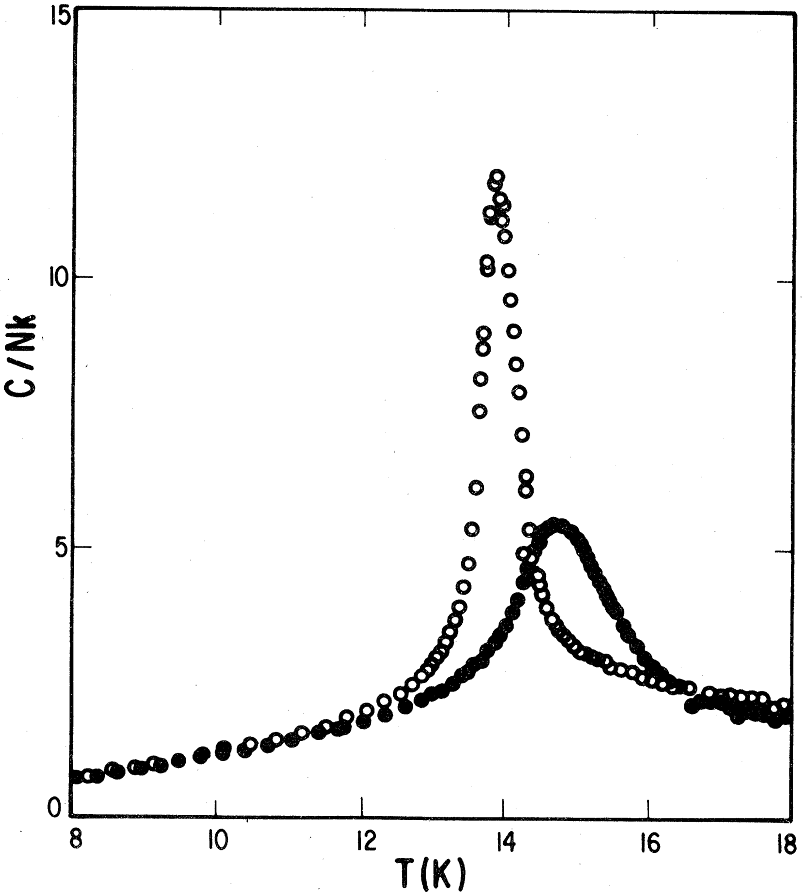

FIG. 5. Heat-capacity measurements as a function of temperature for (○) 0.800 and (●) 0.850 coverages.

developed after going through our first anomaly. We believed that an irregular distribution of the gas was the reason, and we felt that annealing the sample could improve the resolution of our measurements. After a few attempts we found that warming the cell with the gas up to approximately 30 to 40 K (enough to have a pressure in the cell of about 0.5 Torr), and remaining there for more than six hours, made that scatter disappear. We normally left the cell at high temperatures overnight, and then cooled it down before starting measurements. This procedure is described in Ref. 9. The amount of gas that was present in this last operation was always less than 0.3% of the total gas adsorbed for the smaller coverage.

Figure 3 shows the specific-heat measurements for the 0.500 monolayer before (triangles) and after (circles) the annealing procedure. As can be seen, after the annealing procedure the height of the peak increased by a factor of more than 2, and a second peak clearly showed up at about 16 K. All our measurements were made using this annealing procedure.

Heat-capacity measurements were made for coverages 0.100, 0.146, 0.217, 0.320, 0.380, 0.430, 0.480, 0.500, 0.550, 0.590, 0.649, 0.700, 0.800, 0.850, and 0.900 of the monolayer.

Results for 0.217, 0.380, and 0.700 are shown in Fig. 4. Although at 0.100 coverage a not well defined maximum appears and at 0.146 the onset of the first peak is noticed, it is for the 0.217 coverage that we really have a clear first anomaly. The first anomaly remains at $T = (13.57 \pm 0.02)$ K from 0.217 up to 0.650. The width at half-height of these peaks is approximately 0.08 K. The second peak which onset is first seen at 0.146 coverage, clearly appears from 0.217 to 0.550, and from 0.600 on is difficult to see but may still be there. For 0.700 the width of the peak is about 0.1 K; the height starts decreasing and the temperature is slightly higher. From this coverage on, the peak gets rounder and wider as the temperature increases, as can be seen from Fig. 5 which shows the results for the 0.800 and 0.850 coverages.

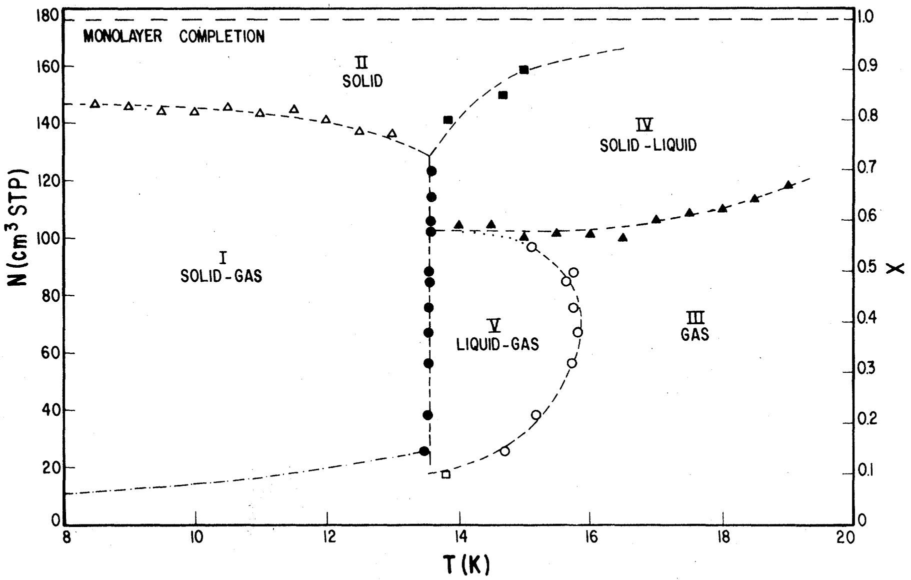

FIG. 6. Two-dimensional phase diagram for neon adsorbed on Grafoil. (Δ) break in isotherm's slopes from Fig. 7; (●) first anomaly in the specific-heat signature; (○) second anomaly in the specific-heat signature; (■) rounded peaks in the specific-heat signature; (▲) low-density ends of the linear portions (corresponding to region IV) of the isotherms from Figs. 8 and 9; (□) maximum at 0.100 coverage; (— • — • —) Huff and Dash (Ref. 2).

Although the peaks at 13.57 K are very sharp, they present finite widths. Due to this width, in principle, we could not consider the corresponding transitions as first-order ones. On the other hand, the constant temperature at which the peaks occur for a large range of coverages strongly suggests the existence of a triple-point temperature. We attribute the finite width to inhomogeneities in the adsorbent surface.

Considering that our first anomaly corresponds to the triple-point temperature and the second to a temperature on the critical curve, we constructed the two-dimensional phase diagram shown in Fig. 6, similar to the one for neon in 3D.

V. TWO-DIMENSIONAL PHASE DIAGRAM

It can be shown[14] that if a two-phase coexistence region exists the heat capacity has a linear dependence on the coverage such that

$$C(N,T)=Nf(T)+g(T) \ ,$$

with N = number of adsorbed atoms, and $g(T)$, $f(T)$, some functions of temperature only.

In order to find the possible coexistence regions in our phase diagram, we built isotherms of C versus N and searched for linear portions. Figure 7 shows some of the isotherms obtained from the heat-capacity measurements. In order to present the isotherms in a clear way, the origin of each one was

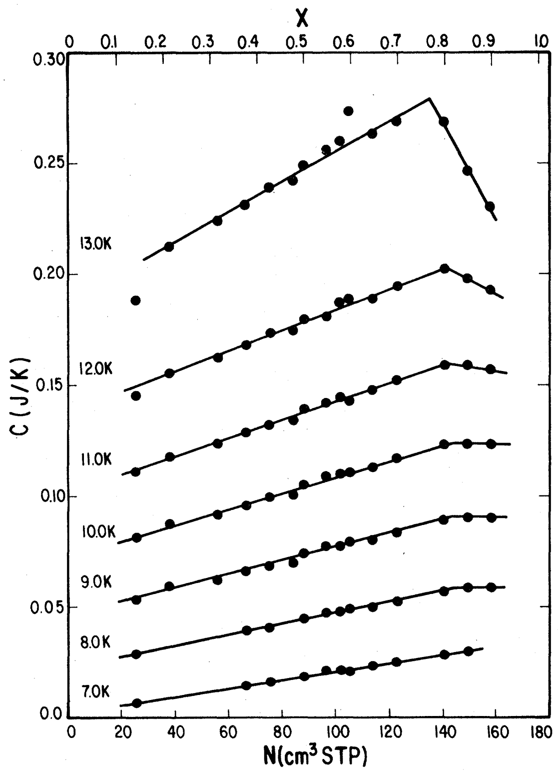

FIG. 7. Isotherms of C vs N from the heat-capacity measurements for temperatures between 7.0 and 13.0 K as marked. To avoid superposition, the origin of each curve, except the bottom one, is displaced by 0.02 J/K relative to the origin of the previous one (see text).

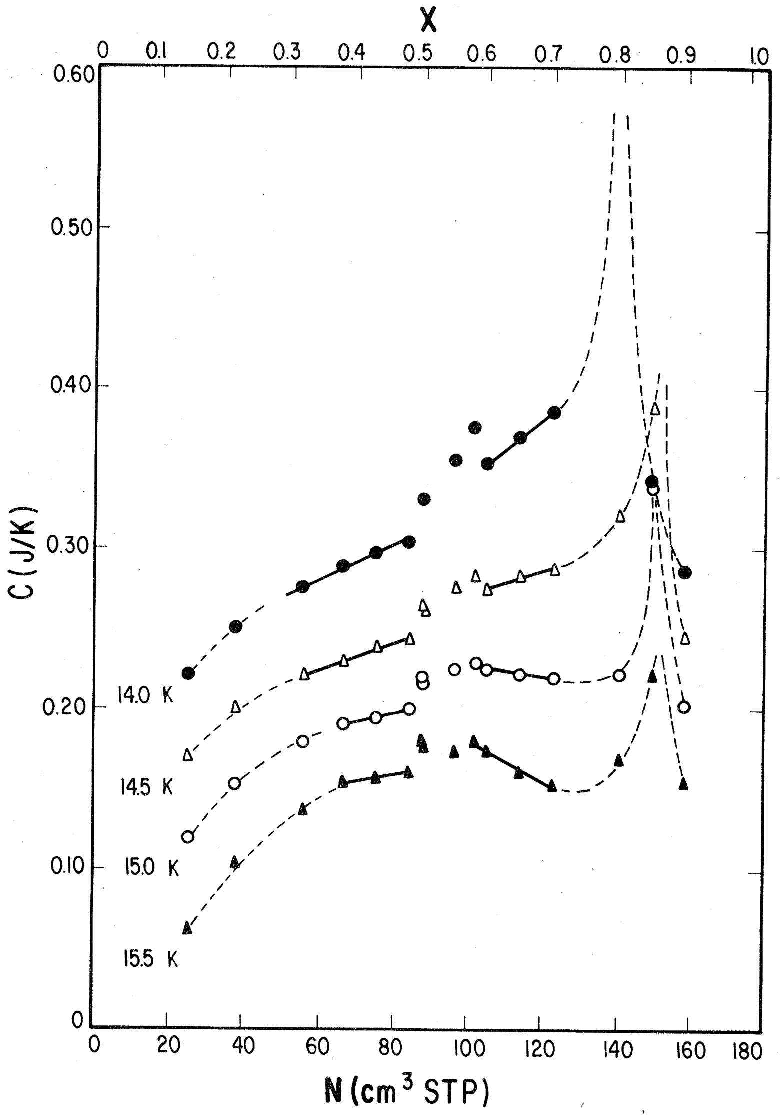

FIG. 8. Isotherms of C vs N from the heat-capacity measurements for temperatures between 14.0 and 15.5 as marked. To avoid superposition, the origin of each curve, except the bottom one is displaced by 0.05 J/K relative to the origin of the previous ones (see text).

displaced by an amount of 0.02 J/K relative to the origin of the previous one, maintaining the origin of the bottom one at its real value on the scale. The linear portions were fitted by least-square fits. It can be seen that for high coverages there are breaks from the linear portions indicating the separation boundary between region I (see Fig. 6), which we believe is the coexistence between solid and gas phases and region II, which we assume to be a solid phase since for low temperatures, between 4 and 10 K, there is evidence of this solid phase with a Debye temperature of about 50 K given in Ref. 2 for the temperature interval 4 to 6 K and in Ref. 15 between 6 and 10 K. For temperatures below 13 K and for low coverages we do not have enough points to determine the boundary line between regions I and III. We can only say that certainly points at 12.0 and 12.5 K for the 0.146 coverage suggest a transition. However, as can be seen from Fig. 7, we cannot establish where the change in the slope occurs. Huff[2] indicates a separation line for regions I and III (shown in Fig. 6) which seems to be too

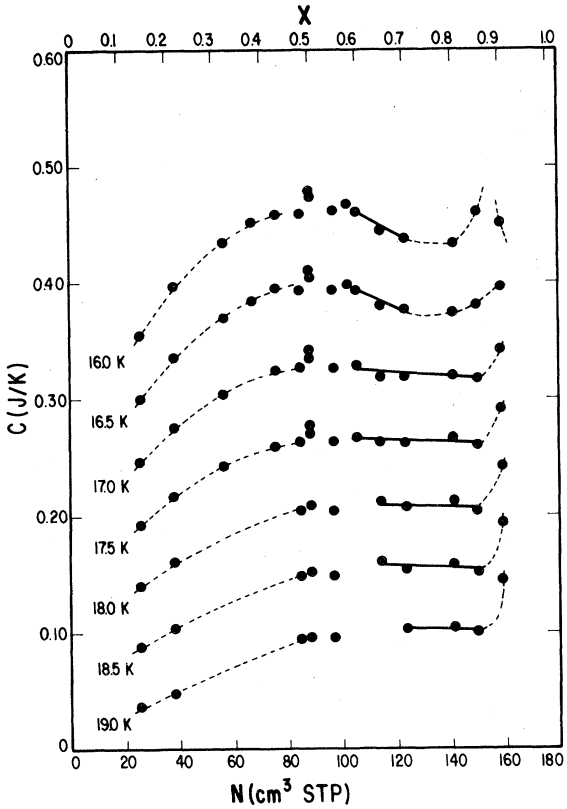

FIG. 9. Isotherms of C vs N from the heat-capacity measurements for $T > 16.0$ as marked. To avoid superposition, the origin of each curve, except the bottom one, is displaced by 0.05 J/K relative to the origin of the previous one (see text).

high in coverage.

For coverages larger than 0.700 the first peaks are smaller and wider with the peak temperature increasing with coverage. This might suggest a "melting line," the solid being transformed into a solid-liquid coexistence phase (region IV).

The coexistence of liquid-gas phases (region V) for temperatures above the triple-point temperature is essential for confirming the assumption of triple and critical curves in our phase diagram. The critical curve (between regions III and V) is obtained from the maximum of the second peaks which are so wide that it is difficult to determine its exact temperature. From the critical curve we determine at its maximum, the critical-point temperature of $T_c = (15.8 \pm 0.1)$ K at about 0.400 coverage. The isotherms of C vs N between 14.0 and 15.5 K, shown in Fig 8, clearly indicate two coexistence regions. Here the same procedure was applied as in Fig. 7 with the difference being that the amount of the displacement was 0.05 J/K. The linear portions on the left of the discontinuity correspond to region V, giving strong support to our assumption of the triple and critical curves obtained from the anomalies in the heat-capacity measurements. The linear portions on the right correspond to region IV, again giving support to our assumption of the existence of a melting region. Isotherms for temperatures higher than 16.0 K, shown in Fig. 9, indicate that region IV extends to higher temperatures, as can be seen from the linear portions. Here the same procedure was applied as in Fig. 8. Taking the left end of these straight lines as the boundary of region IV we obtained the line between regions IV and III. It has to be pointed out that the linear portions of these isotherms, which give evidence of two-phase coexistence regions, do not extend to the limit indicated by the anomalies in the heat capacity. This happens in the gas-(gas-liquid) critical curve and in the solid-(solid-liquid) boundary. This is probably due to substrate inhomogeneities. Due to the same fact, probably the real boundaries between the solid-(solid-gas) regions and the (solid-gas)-gas regions are at higher and lower coverages, respectively, than the ones indicated in Fig. 6. The isotherms below about 0.500 coverage indicate that we have a one-phase region which has to be a gas (fluid) phase in accordance with the rest of the phase diagram. As can be seen from Fig. 9, the tendency of these isotherms, as the temperature increases, is to become a straight line, indicating that the gas tends to be an ideal gas. This can also be seen from the heat-capacity data which tends to the ideal-gas value as the temperature increases.

ACKNOWLEDGMENTS

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