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Adsorption and Specific-Heat Studies of Monolayer and Submonolayer Films of He^3 and He^4†

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A study has been made of the adsorption of He^3 and He^4 at 4°K on a substrate consisting of a monolayer of argon adsorbed on a sintered copper sponge. The isotherms display distinct steps indicating the completion of first and second adsorbed layers. Comparisons among the adsorption isotherms of helium and of Ar and N_2 at 77.4°K yield a self-consistent set of molecular areas. Measurements have been made of the specific heat of five submonolayer coverages of He^3 and He^4 on Ar-plated Cu sponge. The heat capacities of nearly complete monolayers vary as T^2 from 0.3 to 4°K, yielding two-dimensional Debye temperatures $\Theta(He^4)=28\pm1$°K, and $\Theta(He^3)=31\pm1$°K. At lower coverages the molar heat capacities increase and develop contributions linear in T below 1°K. At an intermediate coverage, the heat capacity of He^4 exhibits a broad and pronounced maximum near 3°K. Possible mechanisms for the linear terms and the maximum are discussed briefly. Evidence for considerable mobility of He atoms along the surface is adduced from the temperature and coverage dependence of the heat capacity. The T^2 behavior for the complete monolayers yields an upper limit of $\sim10^{-11}$ sec for the lifetime of a He atom in any individual adsorption site, consistent with a theoretical estimate.

I. INTRODUCTION

Monolayer and submonolayer films of helium adsorbed on solid surfaces at low temperatures are physical systems that combine extremely interesting aspects of surface physics and of the condensed states of helium. In surface physics there are several longstanding questions involving the mobility of adsorbed atoms and of the conditions under which mobile films may undergo varieties of transitions to condensed or immobile states: Use of helium as the adsorbate both enhances the probability of mobile states and also provides more favorable conditions for their detection. For the study of He^3 and He^4, surface films are a domain in which the anomalous properties of the bulk materials are either strongly modified or completely changed by the restriction to two-dimensional phases, but in which certain essential features of their bulk properties may still remain.

Physical adsorption (i.e., surface adhesion of molecules by weak van der Waals forces) has been actively studied for many years, with many combinations of molecular gases and solid substrates, and by a variety of experimental techniques.[1] A major fraction of these studies has employed the method of adsorption isotherms, in which the vapor pressure is measured for varying amounts of adsorbed molecules on an isothermal surface. For several cases of adsorption on highly homogeneous surfaces, the adsorption appears to proceed by the formation of successive atomic layers, each layer being essentially completed before the next begins to form. For less homogeneous surfaces, adsorption appears to proceed at different rates in different regions of the surface. The type of adsorption may often be deduced from the shape of the adsorption isotherm. In some systems there are indications of two-dimensional phase transitions in the films, analogous to the transitions between vapor, liquid, and solid phases of bulk matter. Such transitions have been predicted for many years,[2] but there is still no strong correspondence between the theories and the experimental indications. There are predicted transitions between localized and mobile states of submonolayer films,[3] but no definitive experimental confirmations have been obtained to date.

The properties of He^3 and He^4 have been intensively studied over wide ranges of temperature and density in the gaseous, liquid, and solid states, and they are in large part well understood in terms of theoretical models. However, one class of conditions that has not been adequately explored is the film, especially in the range down to submonolayer coverages. Although mobile He^4 films in contact with bulk liquid were observed long ago and subsequently studied by many workers, these "thick" films are still poorly understood. Thinner films have been studied less intensively, have often yielded conflicting results, and have been subjected to conflicting interpretations.[4] Although experiments on He monolayers are difficult, they are particularly attractive. It is well known that the Bose-Einstein condensation temperature of a two-dimensional ideal gas is suppressed to 0°K.[5,6] It has been predicted that the transition temperature of He^4 films decreases to zero

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[1] For an extensive recent review of experimental and theoretical work on physical adsorption, with emphasis on adsorption isotherms, see D. M. Young and A. D. Crowell, *Physical Adsorption of Gases* (Butterworths Scientific Publications, Ltd., London, 1962).

[2] See, for example, R. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, New York, 1949), 2nd ed., Chap. X.

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[6] R. M. May, Phys. Rev. **135**, A1515 (1964).

when the films are still at finite thickness,[7] and indeed, the onset temperature for superfluidity of He^4 has been seen to decrease with decreasing relative vapor pressure.[8–10] However, recent studies of He^4 adsorption have given indications that there is an apparent transition evidenced by a small step in the adsorption isotherm, and for this step, at an intermediate thickness of 5–10 atomic layers, the apparent transition temperature *increases* as the film is made thinner.[11] In the limit of monolayer and submonolayer films, the superfluid transition may be completely suppressed, but the progressive modifications of the properties as the two-dimensional state is approached, and the modifications imposed by the surface forces are almost completely unknown.

In contrast to He^4, quantum properties of liquid He^3 may be relatively well preserved in ultrathin films. A two-dimensional ideal Fermi-Dirac gas has a condensation temperature approximately one-half of that for a three-dimensional gas of the same density and atomic mass. A recent calculation of the low-temperature properties of He^3 monolayers, using a model potential, indicates a degenerate state having a linear heat capacity and with effective mass m_3^* comparable to that in the liquid.[12] Current experimental studies of thin and monolayer films are not inconsistent with the implication that He^3 monolayers may become statistically degenerate under achievable conditions of density and temperature.[13–15]

It is particularly interesting to study He^3 and He^4 by techniques that are especially useful in answering questions of mobility, phase condensation, and quantum degeneracy. Measurement of the heat capacity is such a technique, and it forms the basis of much of the present work[13–15]; similar studies have recently been described by Thompson.[16] Although it is difficult to obtain significant sensitivity in most other systems of adsorbate gases and solid substrates, the properties of helium, together with the substrates we have employed, have given substantial sensitivity. We have paralleled the specific-heat study with measurements of the adsorption isotherms on the same substrates.[13–15] Each technique yielded information essential to the development of a reasonably consistent outline of the nature of He^3 and He^4 films, from 4 to 0.3°K, and in thicknesses ranging from a few atomic layers to a fraction of a monolayer. Although several features have been explored in detail, many questions remain or have been posed by the results, and these will be the focus of a continuing series of investigations.

II. ADSORPTION SUBSTRATES

The adsorption substrates used in the heat-capacity and adsorption-isotherm experiments were copper sponges coated with monolayers of argon.[14] The argon monolayer capacity and the surface area of the substrate were determined by argon and nitrogen isotherms. The use of sponges was dictated by several requirements: high surface area, rapid thermal equilibrium, and surface homogeneity. Conventional high-surface-area adsorbents[1] are powders or compacts of hard materials such as TiO_2, Fe_2O_3, or graphite, which may be powdered by grinding. Some studies have been carried out on molecular sieves, porous glass, or other solids having unusually open structures. Unfortunately, all of these materials have extremely low thermal conductivities at low temperatures and are therefore unsuitable for heat-capacity measurements. Although at relatively high temperatures thermal equilibrium may be effected by the internal distillation of the adsorbate gas throughout the adsorbent, this is much too slow a process under the conditions present in our experiments, where the maximum vapor pressures were no greater than 10^{-3} Torr, and were usually many orders of magnitude lower. Thermal equilibrium had to be provided by the substrate itself, which could not consequently be a glassy or polycrystalline dielectric.[17,18] Polycrystalline pure metals, on the other hand, have relatively large thermal conductivities at helium temperatures.[17] Except for a geometrical factor due to the pores, the low-temperature thermal conductivity of a metal sponge should be comparable to the polycrystalline bulk metal. Sponges, in which a very high proportion of the powder particles are fused to adjacent particles, are produced by sintering compacted powders at temperatures appreciably lower than the melting point.

The crystal structure of the sponge, at least within a few lattice spacings of the surfaces, is unknown, and may be considerably disordered.[19] Some improvement in surface homogeneity can be provided by preadsorbing an integral number of layers of a gas[20] such as argon, which is more strongly bound to the surface than the

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adsorbate under study. A possible further advantage to the use of argon precoating is the reduction in the helium-surface attraction, which increases the likelihood of surface mobility of the helium. A disadvantage to the use of metal sponges compared to conventional materials is their lower surface area per unit mass and the higher low-temperature heat capacity due to conduction electrons, both of which increase the "background" specific heat of the sponge relative to the signal of the helium. However, it was found that in the present studies the background heat capacity of the calorimeter was of reasonable size in comparison to the signal due to He, even for fractional ($\sim$0.2) monolayer coverage.

We have used as starting material for the sponges commercial copper metallic paint pigment[21] composed of electrolytic copper flakes of irregular shapes, roughly 2 μ on edge and 0.2 μ thick. A description[22] of the preparation and properties of the copper sponges has been given elsewhere, and they will therefore be only briefly described here. Quantities of the powder were first washed in ether to remove organic lubricants remaining from their preparation processes, and then compacted into weighed copper cups with a hand press. The filled cells were then sintered in a tube furnace in purified H_2 atmosphere, usually at 625°C for $\frac{1}{2}$ h. The resulting sponge had a density of 60 to 70% of normal bulk metal, and the appearance of coarse-grained polycrystalline metal. It was firm material, showed no tendency to flake, and was thoroughly bonded to the walls of the cups. The cells were closed with copper caps silver soldered to the cells in He atmosphere. The caps were provided with copper capillary tubing for filling. For adsorption studies, we drilled a small central hole through the sponge after sintering in order to reduce the equilibrium times.

Sponges prepared in this manner have adsorption areas of approximately 50 m^2/mole. The cells used in the adsorption and heat-capacity studies contained about 1 mole of sponge. Details of the adsorption measurements are presented in Sec. III.

III. ADSORPTION ISOTHERMS

A. Experimental Details

An adsorption cell was prepared according to the prescription given in Sec. II. The gas volumetric system consisted of glass storage bulbs, a small calibrated Hg Toepler pump, Hg manometer, and pressure gauges, in an arrangement similar to those conventionally employed for adsorption measurements.[1]

Pressures below 1-mm Hg were measured by means of a thermocouple gauge, calibrated separately for He^3 and He^4 against a McCleod gauge. Thermomolecular corrections were applied according to the formula given by Keesom.[23] Higher pressures were measured with a mercury manometer. The temperature of the liquid-helium bath, in which the cell was immersed, was obtained from measurements of the vapor pressure according to the T_{58} temperature scale[24] and was controlled by means of a mechanical manostat.[25]

B. Nitrogen and Argon Isotherms

Nitrogen and argon adsorption isotherms were taken on the bare copper surface at 77.4°K. The N_2 isotherm [Fig. 1(a)] showed the conventional sigmoid shape of pressure versus quantity of gas admitted to the system, and was analyzed according to the Brunauer-Emmett-Teller (BET) isotherm,[1]

$$\frac{P/q}{V(1-P/q)}=\frac{1}{V_mC}+\frac{C-1}{V_mC}\,\frac{P}{q}, \qquad (1)$$

where P is the equilibrium pressure for a quantity V of gas adsorbed, q is a parameter ordinarily identified as the saturation vapor pressure, V_m is the monolayer capacity, and C is a constant. The BET analysis of the N_2 isotherm yielded a monolayer capacity $V_m=12.6$ cm^3 STP, which implies a BET "standard area," according to the value of 16.2 Å^2/(N_2 molecule),[1] of 55 m^2. However, when the evidence from all isotherms obtained with N_2, Ar, He^3, and He^4 is analyzed consistently, a somewhat lower value is obtained. The complete analysis is presented in Sec. III D. The argon isotherm could not be analyzed in the normal way, because the isotherm intercepted the vapor-pressure line at a finite coverage and at a finite slope [Fig. 1(b)]. Isotherms having such finite intercepts have often been observed; for example, by Singleton and Halsey[26] for Kr on carbon black, and attributed by these authors to an incompatibility between adsorbate and adsorbent lattice structures. We found it possible to represent the major part of the Ar isotherm by modifying the BET Eq. (1) to treat q as an adjustable parameter along with C and V_m. The best fit was obtained with $q=223$-mm Hg (the saturated vapor pressure for solid argon at 77.4°K is 200-mm Hg, while 223-mm Hg is the extrapolated vapor pressure of liquid argon). This gave a V_m which was rather insensitive to the choice of $q=11.9$ cm^3. Halsey has pointed out[27] that the practical utility of the BET formula is that it is an analytic procedure for obtaining for V_m the "point B" of the isotherm, the point at which the "knee" of the curve deviates from the linear portion. Our modification of the equation gave a reasonable fit to the experimental curve, and it yielded a satisfactory "point B."

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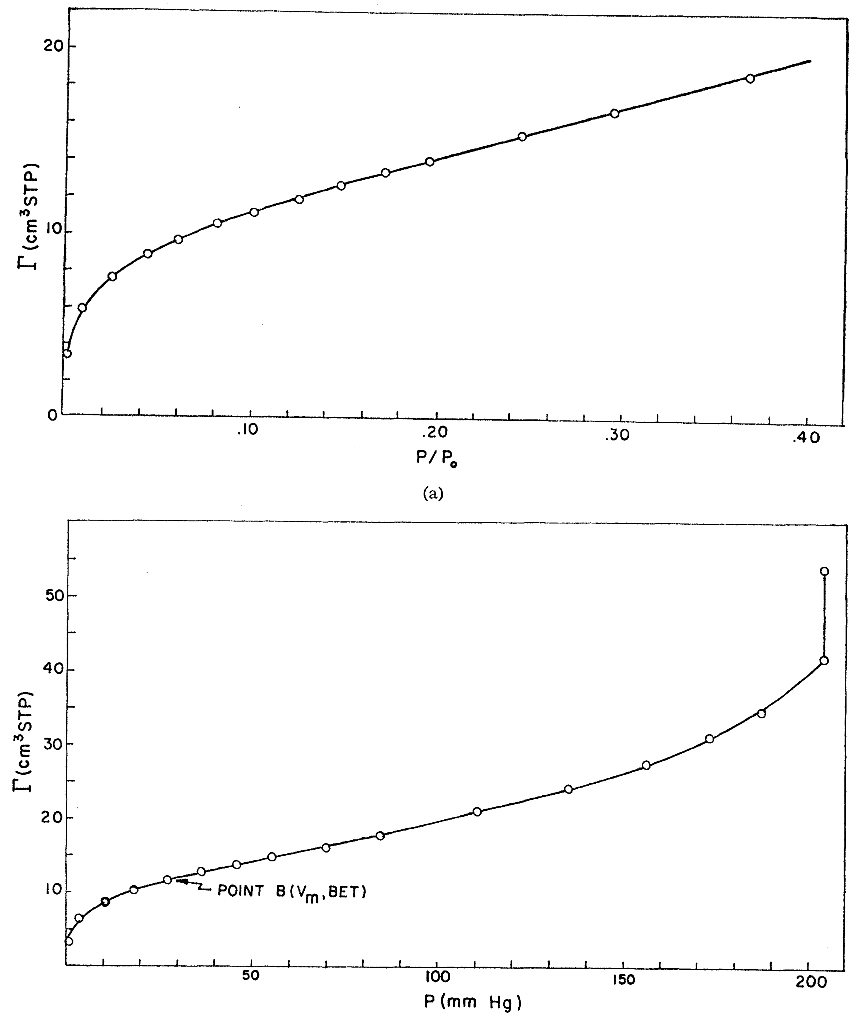

(a)

(b)

FIG. 1. Adsorption isotherms for (a) nitrogen and (b) argon on copper sponge at 77.4°K. (Γ refers to the total quantity of gas admitted to the adsorption cell.)

C. Helium Isotherms

When N_2 and noble gases other than He are adsorbed, monolayers are usually formed at relative pressures $P/P_0 \approx 0.1$. The BET theory may be applied to adsorption data for these gases by plotting $(P/P_0)/[V(1-P/P_0)]$ versus P/P_0 according to Eq. (1). A straight line is usually obtained, and V_m may be deduced. These analyses yield monolayers with densities comparable to the areal density of the bulk liquid. However, early isotherm measurements on helium[4] occasioned a good deal of confusion. They seemed to indicate that the amount of helium adsorbed in a BET monolayer was anomalously large. The basic cause of the difficulty is that the He-adsorbent interaction is so much stronger than the He-He interaction that the equilibrium pressure above a monolayer adsorbed film of helium is very low relative to the vapor pressure of liquid helium.

The problem introduced by the low equilibrium pressures above monolayers of helium was historically compounded by the fact that straightforward application of the BET theory to helium adsorption data in the region of $0.05 < P/P_0 < 0.35$, which is its normal range of applicability, usually yielded very good straight lines. This led many authors to conclude that helium formed extremely dense monolayers, with up to four times the areal density of liquid helium. Later authors have interpreted V_m as representing two or more layers, or as the point at which the excess adsorption energy becomes equal to the thermal energy. Meyer[28] was the first to demonstrate clearly the correctness of this viewpoint. He obtained stepwise isotherms at 2.04 and 4.2°K, showing the formation of the first layer at $P/P_0 \approx 10^{-7}$ and the second layer at $P/P_0 \approx 10^{-4}$. In the present work we find, as does Meyer, that the stepwise isotherms indicate individual layer capacities for the first and second adsorbed layers. A standard BET analysis, when applied to our data,

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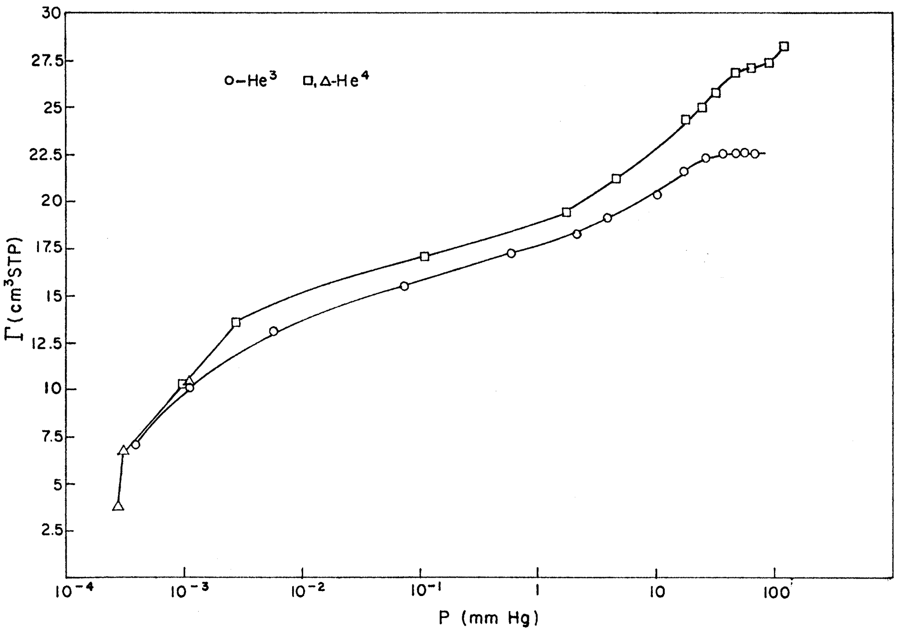

FIG. 2. Adsorption isotherms for He^3 and He^4 on preadsorbed argon at 4.2°K.

yields a straight line, with V_m representing two adsorbed layers.

It is clear that low-pressure data is needed to study helium monolayers. This requirement introduces some acute experimental problems. In conventional adsorption work, reasonable gas pressures serve both to bring the adsorbent-adsorbate system to thermal equilibrium, and to quicken diffusion of the adsorbate into the adsorbent and thus bring about uniform coverage and pressure equilibrium. For helium monolayers on high-surface-area adsorbents at temperatures of 4.2°K or below, there is not sufficient gas pressure to achieve these purposes in a reasonable time. To circumvent these difficulties, Meyer used a low-surface-area adsorbent, gold foil, which would equilibrate in a reasonable time even at very low gas pressures. Hobson,[29] similarly, used a Pyrex cold finger, and also was able to measure much lower pressures and coverages than those accessible to Meyer. Steele and Ross[30] used a relatively high-surface-area absorbent, TiO_2 coated with argon, but made their monolayer studies at elevated temperatures, 10 to 20°K, where there was a substantial vapor pressure above a monolayer. In the present work the use of copper sponge avoided the problems of thermal equilibrium, and required relatively short diffusion times, thus permitting monolayer work with higher surface area than gold foil or Pyrex finger. Furthermore, the relatively low adsorption energy of helium on the argon coated surface made it possible to observe monolayer formation at pressures considerably higher than those observed by Hobson on bare Pyrex.

We measured adsorption isotherms of He^3 and He^4 at 4.2°K over a pressure range of more than six orders of magnitude (Fig. 2). The isotherms form distinct steps, and we interpret these as indicating the formation of distinct layers. The fact that the first layer is formed at much lower pressure than the second implies that the binding energy in the first layer is much greater than in the second. Furthermore, the low vapor pressure of the second layer indicates that the binding energy in even the second layer is appreciably greater than in the liquid. The low coverage data may be analyzed by means of the Langmuir isotherm,[1]

$$P/V=k/V_m+P/V_m, \tag{2}$$

which implies a single homogeneous layer capacity V_m with a uniform binding energy, and no possible further adsorption. It may therefore be applied to stepwise isotherms in the intervals corresponding to the formation of each discrete layer. The applicability of this isotherm indicates that the first layer is essentially complete before the second begins to form. Plots of P/V versus P for the first layers of He^3 and He^4 are shown in Fig. 3. Analysis yields first-layer capacities of 14.1 cm^3 STP for He^3 and 15.8 cm^3 STP for He^4.

Since the difference in binding energy between the second and third layers is much smaller than between the first and second, it is now possible to apply ordinary BET analysis to the second layer of He^4, after subtracting off the first-layer capacity; in other words, the second layer is considered to be adsorbed on a substrate of He^4. This procedure was also followed by Dacey and Edwards[31] and by Brewer and Champeney.[32] This second-layer BET plot is shown in Fig. 4(a). There results a second-layer capacity of 11.2 cm^3 for He^4. The

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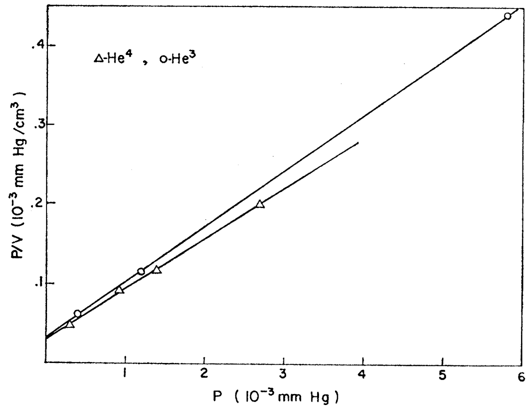


FIG. 3. Langmuir plots for the first layers of He^4 and He^3 on preadsorbed argon at 4.2°K.

second-layer data for He^3 cannot be analyzed by the conventional BET method because the temperature of the isotherm, 4.2°K, is above the critical temperature of He^3. However, there is no further increase in adsorption after the second layer has been formed (Fig. 2), and so the Langmuir isotherm is again applicable for the second layer of He^3. The fit to the Langmuir isotherm is shown in Fig. 4(b): This curve also illustrates the fact that the Langmuir isotherm is not applicable to the second layer of He^4 because multilayer adsorption takes place. The second-layer capacity for He^3 is 9 cm^3 STP.

The results of this analysis of layer capacities are summarized in Table I. It may be seen on comparing the He^3 and He^4 values to Fig. 2 that these agree with the positions of the steps in the isotherms.

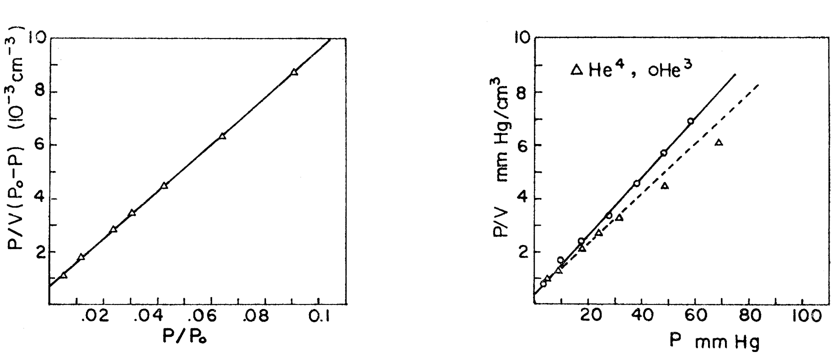
As the thickness of the adsorbed film increases, the binding energy between the surface and the top of the film falls off as the third power of the film thickness. If one assumes that the film thickness is proportional to the number of layers adsorbed, one obtains

$$-\ln(P/P_0)=b/RT\theta^3, \tag{3}$$

where θ is the number of layers adsorbed and b is a constant. This expression is known as the Frenkel-Halsey-Hill isotherm.[33] If the layer capacities are known, a plot of $-\ln(P/P_0)$ versus θ^{-3} should yield a straight line through the origin for coverages high enough to justify the assumption of a planar adsorbent. In Fig. 5 our data are plotted in this manner, making use of the layer capacities in Table I. The straight line is given by

$$P/P_0=\exp(-172/RT\theta^3). \tag{4}$$

Meyer[28] has suggested that for helium isotherm data at relative pressures above 0.05, BET analysis chooses as V_m that coverage at which $(E_a-E_0)\simeq RT$, where E_a is the adsorption energy and E_0 the latent heat of vaporization of bulk liquid. This interpretation explains both the large magnitude and the variation with temperature usually found for V_m. When our high-pressure ($P>1$-mm Hg) data for He^4 are analyzed according to BET, we obtain $V_m=28$ cm^3 STP. The excess binding energy as a function of coverage may be deduced from Eq. (4) and is equal to RT at $\theta=2.6$ or 34 cm^3 STP adsorbed. Since this number is extremely sensitive to the binding energy, varying as $E_a{}^3$, this agreement is not entirely satisfactory. On the other hand, 28 cm^3 STP agrees very well with the combined capacity of the first two layers from Table I, 27 cm^3 STP. Part of the reason for this is illustrated by the present data for He^3. In this case there is no further adsorption after a coverage of 23.2 cm^3 STP has been reached. When data for which V has become independent of P is analyzed by the Langmuir isotherm Eq. (2), the resulting V_m is necessarily equal to V, and thus $V_m=23.2$ cm^3 STP correctly gives the combined capacity of the first two layers. A previous study[34] of adsorption of He^3 and He^4 on charcoal has similarly shown BET monolayer capacities appreciably smaller for He^3 than for He^4. In the case of He^4, where multilayer adsorption takes place, V continues to rise slowly with P. The BET isotherm balances this by the variation of $(1-P/P_0)$ in the denominator of the left-hand side, and gives a straight line, but the value of V_m is still governed by the onset of the plateau (i.e., by point B). If the adsorption energy



(a) (b)

FIG. 4. (a) BET plot for the second layer of He^4 at 4.2°K. No BET plot is possible for He^3 above the critical temperature. (b) Langmuir plots for the second layers of He^4 and He^3.

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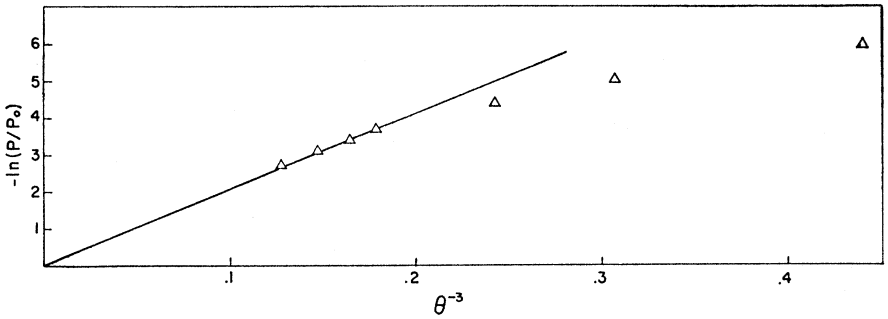

FIG. 5. Frenkel-Halsey-Hill plot, He^4 on preadsorbed argon at 4.2°K. Ordinate is in layers, with layer capacities deduced from Langmuir first-layer and BET second-layer analyses.

E_a as a function of coverage is reasonably smooth and structureless, then the isotherm will have no features characteristic of layer formation and the plateau and apparent point B depend largely on where the relative pressure reaches the normal BET range of applicability, $0.05<P/P_0<0.35$. This is clearly related to Meyer's conditions $(E_a-E_0)\simeq RT$. To state the case differently, if a logarithmic plot of an isotherm of the type shown in Fig. 1 is a smoothly increasing curve without structure, then any small portion of the curve plotted on a linear scale shows a characteristic plateau and point B. The same portion of the data under BET analysis gives a V_m which is governed by the pressure range chosen rather than any property of the physical system. Meyer's condition represents recognition of the particular pressure range chosen by most previous authors. If, on the other hand, the helium-adsorbent system forms a series of distinct layers, characterized by distinct steps in the isotherm as in Fig. 1, which in turn reflect steps in E_a as a function of coverage, the plateau and point B will depend on the layer capacities, and the application of the BET equation to any given plateau region will result in a V_m which is the total capacity of an integral number of layers.

Hobson's measurements of the adsorption of He^4 on Pyrex at very low pressures gave evidence (though not conclusive) that at 4.2°K a monolayer is formed at a relative pressure $P/P_0\sim 10^{-12}$. From this he deduced a lower limit on the adsorption energy $E_a\geq 250$ cal/mole, and he pointed out that measurements on other substrates have indicated that this number can be as high as 700 cal/mole. Steele and Ross, working on argon-coated TiO_2, measured an adsorption energy $E_a\leq 200$ cal/mole at the completion of the first layer. Direct comparison of our isotherm to that of Steele and Ross at the same temperature (Fig. 6) indicates that the adsorption energy is lower in our system; thus we can place an upper limit of 200 cal/mole on the energy governing the completion of our monolayer. If one writes very roughly that at the point where the monolayer is completed, $-\ln P/P_0\simeq E_a/RT$, then Hobson observes approximately 28 for this number, and we observe approximately 14 or about half the binding energy. This is consistent with our observation that the first monolayer of He on Ar-coated Cu is formed at $P/P_0\approx 10^{-6}$.

D. Discussion of Isotherms

There is an extensive literature[1] on various experimental and analytical methods for determining adsorbent surface areas from measured V_m values, but a considerable uncertainty still remains. A conventional

TABLE I. Monolayer capacities V_m for adsorption cell and calculated equivalent molar volumes for complete monolayers. Nitrogen and argon are at 77.4°K and He^4 and He^3 at 4.2°K. The tabulated values are obtained by scaling monolayer capacities V_m relative to $V_m(N_2)$; $\sigma_m(N_2)_{\text{solid}}=13.8$ Å²/molecule and $\sigma_m(N_2)_{\text{liquid}}=16.2$ Å²/molecule.[a]

	V_m (cm³, STP)	Equivalent molar volume (cm³ STP)		Molar volumes of bulk liquid and solid at temperatures and pressures indicated (cm³/mole)
		$\sigma_m(N_2)_{\text{solid}}$	$\sigma_m(N_2)_{\text{liquid}}$	
N_2	12.6			
Ar	11.9	29.5	37.6	Liquid: 28.3 at 86°K, 1 atm Solid: 24.2 at 40°K, ~0 atm
He^4 (1st layer)	15.8	19.3	24.6	hcp solid: 19 at 2.7°K, 63 atm Liquid: 19 at 3.5°K, 100 atm
He^4 (2nd layer)	11.2	32.2	41.1	Liquid: 32. at 4.2°K, 1 atm
He^3 (1st layer)	14.1	22.9	29.1	Liquid: 22.7 at 2.1°K, 65 atm 22.6 at 3.3°K, 70 atm
He^3 (2nd layer)	9.0	44.9	57.0	Liquid: 43.3 at 2.9°K, 1 atm 42.3 at 3.3°K, 2 atm

[a] Reference 33.

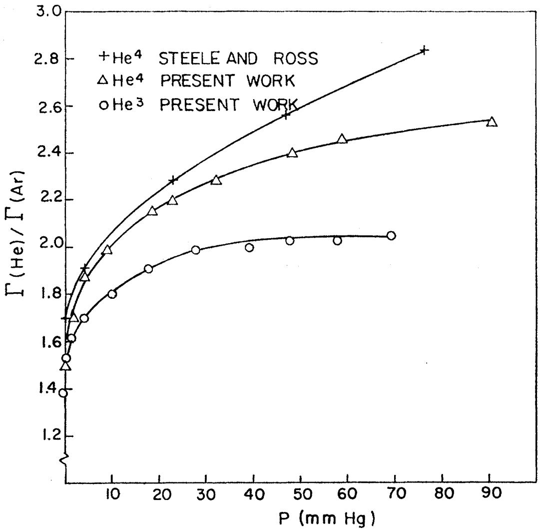

FIG. 6. Adsorption isotherms for helium on preadsorbed argon at 4.2°K.

procedure yielding the "BET standard area" from N_2 isotherms at 77.4°K has the advantage of simple analysis from easily obtained data. Although treated as a reference standard, the BET standard area may in some cases be considerably different from areas measured by other techniques, or from isotherms obtained with other gases. The basis for the convention is the use of the molecular area $\sigma_m \approx 16.2$ Å^2/(N_2 molecule), corresponding to liquid-N_2 density at the normal boiling point.[35] However, isotherms of Ar and Kr on TiO_2 and other adsorbents, when analyzed according to the BET standard method, yield values for their molecular areas which are consistently larger than those corresponding to their liquid densities at normal pressures and temperatures, whereas rather smaller molecular areas are to be expected, because the adsorbate-adsorbent attractive energies are larger than the binding energy of atoms in the liquid. The discrepancies are usually resolved by using "corrected" values for the molecular areas σ_m of Ar, Kr, and adsorbates other than N_2. The correction factors depend upon both adsorbate and adsorbent: For TiO_2 surfaces, they are 0.70 for Kr and 0.77 for Ar. An alternative method for achieving consistency among the N_2 Ar, and Kr measurements would be to use a smaller value for $\sigma_m(N_2)$, but no single choice can resolve the discrepancies for all surfaces. We find a similar discrepancy between the N_2 and Ar isotherms in the present study, and it could be resolved by applying a correction factor for Ar comparable with those previously used. However, we have chosen instead to use the smaller value $\sigma_m(N_2) = 13.8$ Å^2 corresponding to solid N_2.[35] This choice has the important added advantage in yielding physically more reasonable values for the density of He monolayers. With the smaller value of $\sigma_m(N_2)$, the second-layer densities of both He^3 and He^4 correspond closely to bulk liquids, whereas the densities calculated according to $\sigma_m(N_2) = 16.2$ Å^2 yield a second-layer density for He^4 falling 13% *lower* than the saturated liquid at 4.2°K. On the contrary, we expect the density of completed layers to be *greater* than in bulk liquid at the same temperature. In Table I we list the values of σ_m for Ar and for individual first and second layers of He^3 and He^4 calculated according to each choice of $\sigma_m(N_2)$. With $\sigma_m(N_2) = 13.8$ Å^2, we find that the density of the second layer of He^4 at 4.2°K corresponds to bulk liquid at the normal boiling point,[17] while the first layer has the density of hcp solid He^4 at 4.2°K and 65 atm.[36,37] The ratio of effective pressures in the two layers is consistent with the assumption that the principal contribution to the binding energy of a layer is due to van der Waals attraction to the solid substrate. For uniform layer spacing and a smooth substrate, the van der Waals force varies as the fourth power of the inverse layer number: Interactions between layers will reduce the steepness of the decrease, while a greater second-layer spacing will increase it. We cannot analyze the He^3 second-layer densities by comparisons with bulk liquid at 4.2°K since this is higher than the critical temperature. Comparison to liquid He^3 densities at lower temperatures[38] yields an equivalent pressure on the first layer of about 65 atm, comparable to that on the first layer of He^4.

IV. HEAT CAPACITY

A. Experimental Technique

The calorimeter consisted of a thin-walled copper cylinder filled with copper sponge prepared according to the same prescription used for the adsorption cell.[13–15] BET analysis of adsorption isotherms at 77.4°K gave a monolayer capacity for the calorimeter sponge of 8.4 cm^3 STP for both argon and nitrogen, corresponding to He^3 and He^4 monolayer capacities of 9.4 cm^3 STP and 10.5 cm^3 STP, respectively. A computational error led to somewhat higher monolayer capacities quoted in an earlier publication.[13] The volume of the sponge was 10 cm^3.

In order to assure a clean, uniform surface for helium adsorption, 1.2 monolayers of argon were measured into the calorimeter along with each charge of helium. The calorimeter was then sealed off and mounted in the heat-capacity cryostat. During the gradual cool-down before each run, the argon, because of its much greater adsorption energy, was completely preadsorbed before any of the helium adsorbed. Thus, the immediate substrate for the helium adsorbate was actually argon.

Above 1.2°K, the sealed calorimeter was cooled via

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[35] See Ref. 1, pp. 226–239.

[36] E. C. Heltemes and C. A. Swenson, Phys. Rev. **128**, 1512 (1962).

[37] D. O. Edwards and R. C. Pandorf, Phys. Rev. **140**, A816 (1965).

[38] R. H. Sherman and F. J. Edeskuty, Ann. Phys. (N. Y.) **9**, 522 (1960).

an exchange-gas link, by a He^4 bath, and isolated before each point was taken. Adiabatic demagnetization of 25 g of potassium chromium alum was employed for refrigeration below 1.2°K. The paramagnetic salt pill was thermally connected to the calorimeter by means of a superconducting lead heat switch. This heat switch, whose thermal conductivity could be continuously varied,[39] made possible cancellation of the temperature drift due to stray heat inputs and allowed essentially isothermal calorimetry over the entire operating range.

The temperature was measured by monitoring the resistance of carbon composition resistors cemented into copper sleeves soldered to the calorimeter. A 100-Ω Speer resistor was used below 1.2°K and a 56-Ω Allen Bradley resistor between 1.2 and 4.2°K. The resistance thermometers were measured with an ac Wheatstone bridge of conventional design operating at a frequency of 30 Hz, phase locked to the line frequency.[40] The bridge null indicator was a low-noise narrow-band amplifier followed by a phase-sensitive linear detector whose output was displayed on a chart recorder. The measuring power in the carbon resistor was always low enough to avoid self-heating errors and was typically between 10^{-11} and 10^{-8} W, depending on the temperature and which resistor was being measured. The electrical noise of the bridge was such that even at the lowest temperatures when the smallest measuring voltages were used, the temperature could be read with a precision of 0.025%. Thus when a typical $\Delta T/T$ of 5% was used for a specific-heat point the electrical noise never contributed an error of more than 0.5%. On a separate run with the heat switches shorted the resistance thermometers were calibrated against the He^4 vapor pressure (T_{58} scale) and the magnetic susceptibility of the paramagnetic salt.

The susceptibility of the paramagnetic salt was measured by means of the 33-Hz mutual-inductance bridge shown in Fig. 7. The null detector was of conventional design, consisting of a narrow-band amplifier and phase-sensitive detector whose reference signal was taken from the audio oscillator driving the bridge. The secondary of the mutual-inductance transformer was matched to the high-impedance input of the amplifier with a high-turns-ratio transformer to improve the signal-to-noise ratio. Because of the geometry of the apparatus, when one of the secondary coils surrounded the salt pill the other coil was partially occupied by the sponge. This created a spurious imbalance in the bridge which, however, because the resistance of the copper was essentially constant, varied little between 4.2 and 2.5°K and not at all below 2.5°K. Because of eddy-current losses in the sponge, the apparent susceptibility was complex and had to be balanced by a capacitor in parallel with the appropriate resistor in the bridge. The out-of-phase current necessary to balance the bridge was less than 1% of the in-phase current.

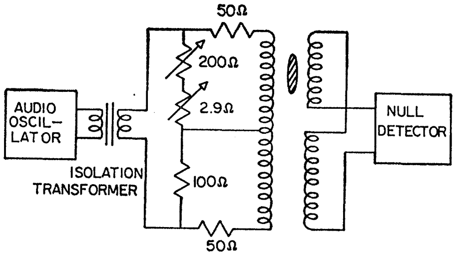

FIG. 7. Mutual-inductance bridge.

The heater was made of Evanohm wire varnished onto the outside of the calorimeter, and had a resistance of 100Ω. Electrical leads were thermally anchored at the salt pill. The heater leads between the salt pill and calorimeter were coated with superconducting Pb-Sn solder. After each heating period, the calorimeter had a thermal relaxation time of less than 7 sec, regardless of filling, at all temperatures. The heater current and voltage were measured with a Leeds and Northrup Type 8687 potentiometer and a precision wire-wound resistor in series with the heater. The heater current was switched on manually, and turned off by a relay operated automatically when a preset scalar had counted a predetermined number of 120-Hz pulses derived from the line frequency.

The data reduction was accomplished in the following way: The resistance change corresponding to a given specific-heat point was measured from the chart-recorder trace by the usual technique of extrapolating the drift rates before and after heating to the midpoint of the heating period. A sample heating curve is shown in Fig. 8. The data recorded for each specific-heat point were the chart-recorder voltage change, the value of the bridge-balancing decade resistor, the heater power, and the time for which it was on. A calibration of chart-recorder output for each point was obtained by switching the decade resistor. These data together with the calorimeter charge and the thermometer calibration parameters were punched onto cards and the calculation of the specific heat at each point was performed by an IBM 7090 computer. The computer was also programmed to perform a least-squares fit of various polynomials to the resulting calculated values of specific heat as a function of temperature.

The empty-calorimeter heat capacity formed the background for all the other data taken, constituting from 70 to 95% of the total heat capacity. It was measured twice, in nonconsecutive runs, with and without a monolayer of argon, and the data were least squares fit to a fourth-order polynomial. The rms fractional deviation of the second-run data from the polynomial derived from the first run was about the same as the rms deviation of the first run from that data, amounting to about 1.4%.

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[39] J. G. Dash, D. L. Goodstein, and W. D. McCormick, Cryogenics **6**, 241 (1966).

[40] The advantage of this mode of operation has been discussed by N. T. Larsen, Rev. Sci. Instr. **33**, 1200 (1962).

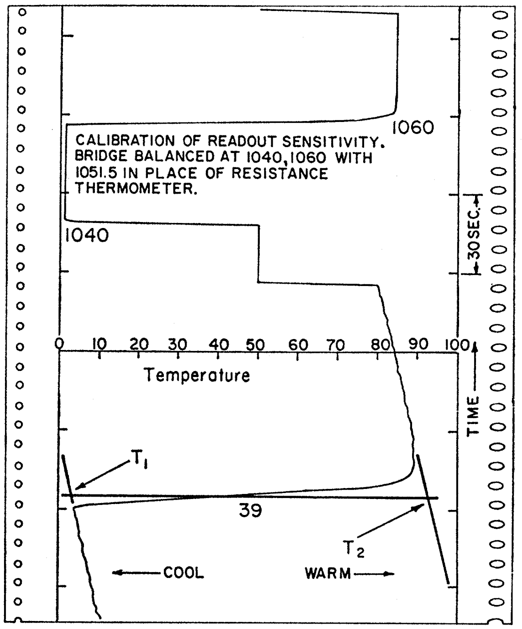

FIG. 8. Chart-recorder trace for a typical heat-capacity point.

The helium isotherms were analyzed to see if it was necessary to make desorption corrections to the measured specific heat. It was found that even at the highest temperatures there was always less than one part in 10^4 of the sample in the gas phase and that such corrections were unnecessary.

TABLE II. Calorimeter charges for specific-heat measurements and derived quantities. Full monolayers for this calorimeter were calculated from nitrogen isotherms to be 10.5 cm^3 STP for He^4 and 9.4 cm^3 STP for He^3.

	He^4			He^3	
Calorimeter charge in cm^3 STP	8.29	6.54	3.23	8.09	4.6
Fraction of a monolayer at 4.2°K	0.79	0.62	0.31	0.86	0.49
Area per molecule σ in Å^2 for $\sigma_m(N_2)=13.8$ Å^2/molecule	14.0	17.7	35.9	14.3	25.2
Mean He-He spacing ($\sigma^{1/2}$) in Å	3.7	4.2	6.0	3.8	5.0
Equivalent molar volume in cm^3/mole	27.6	39.5	70.9	28.6	66.9

B. Experimental Results

Heat capacities were measured for the five coverages shown in Table II. The table shows the measured calorimeter charge, which is proportional to the number of moles, and also various derived quantities which have been calculated using the results of the adsorption measurements. It is worth emphasizing that the monolayer fraction is the fraction of the 4.2°K monolayer capacity. The monolayer capacity is generally a function of temperature,[28] increasing at lower temperatures; hence one monolayer or less coverage at 4.2°K can never become greater than a monolayer at low temperatures.

The specific heats for nearly complete monolayers of both He^3 and He^4 are shown in Fig. 9(a). These curves may be fitted by the following expressions:

$$C/nR\ (\text{Curve I, He}^3)=(0.030\pm0.003)T^2,$$

$$C/nR\ (\text{Curve II, He}^4)=(0.038\pm0.003)T^2,\quad 0.25°\text{K}<T<3°\text{K}.$$

To make the quadratic temperature dependence clearer,

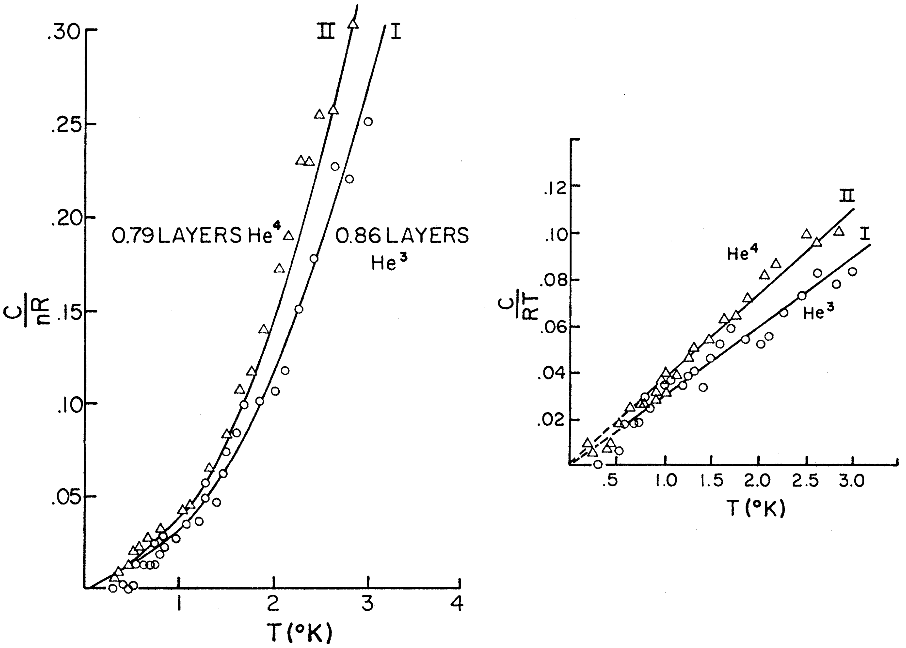

FIG. 9. Specific heats of nearly complete monolayers of helium on preadsorbed argon.

in Fig. 9(b) the same data have been plotted as C/nRT versus T.

At lower coverages the heat capacity per atom increases markedly and the temperature dependence is no longer quadratic. The results are shown for He^4 in Fig. 10 and for He^3 in Fig. 11.

The scatter in measurements of the total heat capacity, empty calorimeter plus helium charge, was 1 to 2%. This was mainly due to uncertainty in extrapolation of the drift rates which were irregular due to small stray heat inputs probably caused by vibrations. The fractional scatter was, of course, amplified by subtraction of the smoothed empty-calorimeter heat capacity. The estimated maximum systematic error in the heat capacity of the adsorbed helium due to uncertainty in the heater resistance and to the empty calorimeter subtraction was 1%, and the maximum uncertainty in the helium charge was 2%.

C. Interpretation of Results

The high coverage data for both He^3 and He^4, which both show T^2 behavior, strongly suggest an interpretation in terms of the two-dimensional Debye model. At temperatures small compared to the Debye temperature this model gives a molar specific heat $C=28.8R(T/\Theta)^2$. The experimental values for Θ are 31±1°K for He^3 and 28±1°K for He^4.

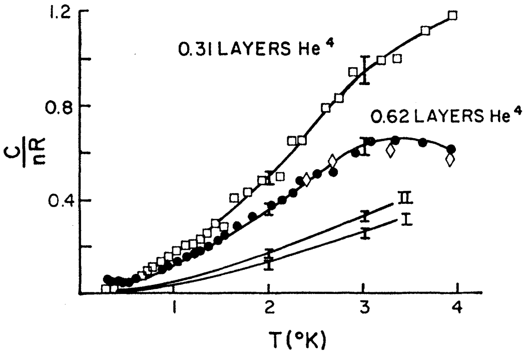

FIG. 10. Intermediate- and low-coverage specific heats for He^4. Curves I and II show the smoothed high-coverage data for He^3 and He^4.

Brewer *et al.*[41] have reported seeing a quadratic dependence for the specific heat of a monolayer of He^4 adsorbed within the pores of Vycor glass. Although the measurements were made at about 50% higher areal density than the experiments reported here, they also find a Debye temperature of 28°K. The temperature range of their measurements was not indicated. Our values for the Debye temperature are surprisingly high considering that the mean interparticle spacing (see Table II) corresponds, in the case of He^4, to bulk liquid at the vapor pressure, and for He^3, to liquid at about

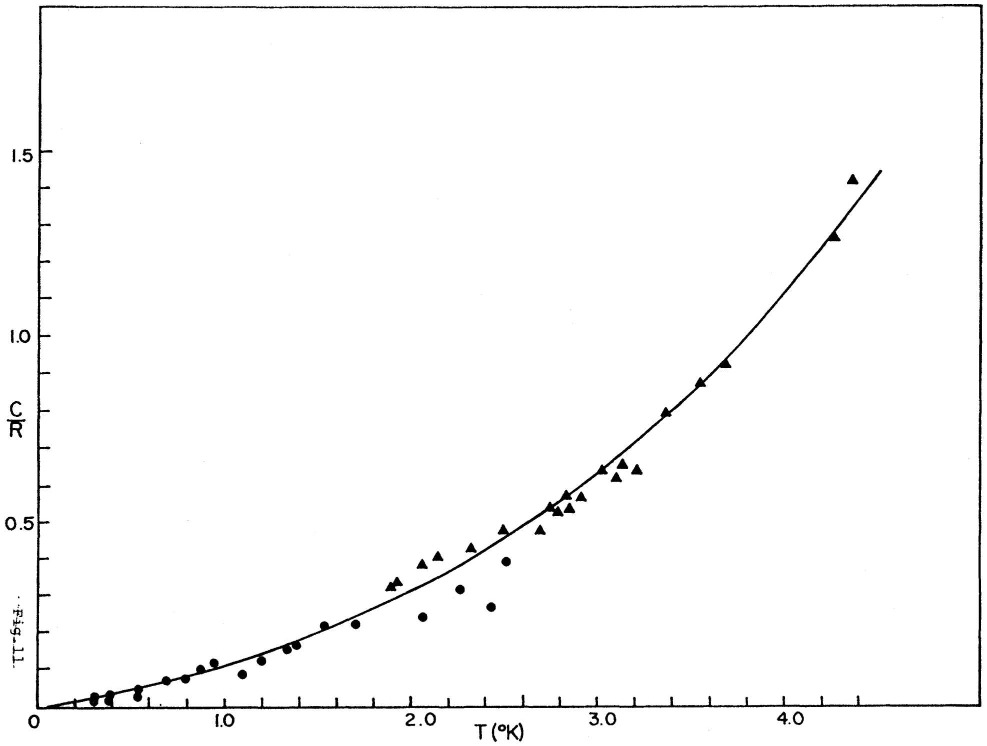

FIG. 11. Intermediate-coverage specific heat for He^3.

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[41] D. F. Brewer, A. J. Symonds, and A. L. Thompson, Phys. Rev. Letters 15, 182 (1965).

15-atm pressure. Conversely, bulk solid He^4 and He^3 having characteristic temperatures of about 30°K are appreciably more densely packed than the monolayers which have such Θ's. Because of geometrical restrictions hindering the atomic motions, however, it should not be surprising to find a solid in two dimensions at atomic spacings corresponding to a liquid in three dimensions. It is also possible that the dependence of the helium-substrate interaction potential on position might produce some "steric hindrance," and cause "melting" to occur at a lower density than that found in three dimensions.

The qualitative features of the experimental heat capacities indicate considerable lateral mobility of the adsorbed He, and this is particularly evident at submonolayer coverages. The dramatic increase in molar specific heat can be seen by comparing curves II, III, and IV of Figs. 9 and 10: respectively, 0.79, 0.62, and 0.31 monolayers of He^4; Fig. 11 illustrates similar behavior for low-coverage He^3. The low-coverage results show heat capacities per He atom that are strongly dependent on coverage over the entire temperature range. Strictly localized and noninteracting He atoms would have molar specific heats independent of coverage. Although long-range He-He interactions would produce some variation with coverage, they are unlikely to play an important role here. At 0.3 monolayers the mean distance between neighboring He atoms is approximately 6 Å, and the He-He pair interaction energy is about 0.1°K.[42] It is unlikely that the He-He interaction could be enhanced by interactions with the substrate to the extent necessary to account for the observed coverage dependence. Such an enhancement would require relatively important rearrangements of the Ar layer in the vicinity of an adsorbed He atom, and this seems to be ruled out because the He-Ar interaction is much smaller than the Ar-Cu interaction.

Further evidence against localized adsorption is obtained by examining the temperature dependence. For localized adsorption, the variation of heat capacity with temperature depends upon the shape of the potential wells at the adsorption sites. Under the conditions of the present experiments, however, we can deduce the temperature dependence for any well shape. The quantum states of localized atoms are characterized by energy-level separations $\approx h^2/md^2$, where m is the mass of the He atom and d is the "size" of the site. For $d=2.5$ Å, approximately one-half of the Ar-Ar distance, the separation corresponds to about 2.5°K. Larger values of d would contradict the assumption of localization. Therefore, over much of the experimental temperature range, only the ground state and first excited states of localized He atoms could be significantly occupied. This situation yields an exponential dependence on temperature, of the form $C\propto \exp(-\Delta/T)$. The observed heat capacity, on the other hand, shows no apparent exponential behavior for any coverage, down to the lowest temperatures.

The high-coverage T^2 specific heat is further evidence that the forces which tend to localize the He atoms at certain sites on the Ar layer do not dominate the dynamics of the He. If the He atoms can tunnel rapidly from site to site, then density fluctuations can be relaxed by this mechanism, and phonons will be a good description of the excitations of the system, so long as their frequencies are small compared to the inverse tunneling time. For a Debye spectrum, the important phonons contributing to the heat capacity at some temperature T are those with frequencies $\nu=kT/h$. For the temperature range of these experiments, the appropriate frequencies range from 4×10^9 to 8×10^{10} Hz. These phonon frequencies are consistent with the estimate of tunneling times between surface sites as low as 10^{-11} sec.[43]

Within the framework of the Debye model, phonons of the Debye frequency have a wavelength of the order of the mean interparticle separation. For the coverages used in these experiments, this results in a wavelength of about 1000 Å for the phonons which dominate the specific heat at 0.2°K. Although large on a microscopic scale, this wavelength is still a factor of 10 smaller than the particle size used to make up the adsorption substrate. Nevertheless, it is surprising to find collective behavior extending over such large distances. Since the wavelengths of the excitations producing the observed specific heat are much larger than the mean spacing between helium atoms, there is no indication as to the degree of local order present. Further investigation of the heat capacity as a function of coverage is necessary before a more detailed model can be tested, but the general features of two-dimensional solidlike behavior is clear.

An extremely interesting feature of these specific-heat results is the broad maximum at about 3.3°K for the intermediate coverage He^4 (Fig. 10, curve III). One possibility that suggests itself is that this is due to a diffuse melting transition between a disordered solidlike and a liquidlike surface phase.

Although the small signal-to-background ratio for the lowest coverages has led to moderately large scatter of points, there appears to be a linear term in the heat capacity of both He^3 and He^4 (see Figs. 10 and 11). Such a linear dependence is suggestive of the heat capacity of two-dimensional Bose and Fermi gases at low temperatures.

ACKNOWLEDGMENTS

The authors gratefully acknowledge many valuable discussions during the course of this work with Professor G. D. Halsey and Professor R. E. Peierls. We are also grateful to G. A. Stewart for his technical assistance.

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[42] J. L. Yntema and W. G. Schneider, J. Chem. Phys. 18, 641 (1950).

[43] J. G. Dash, J. Chem. Phys. (to be published).