Some Experiments on Flow in the Unsaturated Helium II Film

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The mass flow in adsorbed layers of helium has been measured. Superfluidity occurs at all temperatures below the λ-temperature of the bulk liquid down to $1\frac{1}{2}$ statistical layers. The bearings of these results on the thermodynamics of transition HeI−HeII in adsorbed layers is discussed.

THE existing data on multilayer adsorption of helium at temperatures below 4.2°K,[1] show that adsorbed layers of helium exhibit unusual properties, as compared to the behavior of other adsorption systems.

The first adsorbed monolayer is very highly compressed,[1] the density varying from about twice that of the bulk liquid at 4.2° to almost four times the liquid

FIG. 1. Apparatus for measuring mass flow in adsorbed layers of helium resulting from pressure gradients.

density at temperatures below 2.19°. The properties of this first layer resemble those of solid helium under high pressure.[2]

The adsorption in the He II region, below 2.19°K, is anomalously high, and only slightly temperature-dependent, so that the heat of adsorption is not much different from the heat of vaporization of the bulk liquid, even at fairly low coverage.

In the course of the work of Long and Meyer,[1] some measurements on the distribution of He^3 between adsorbed film and vapor at various temperatures and saturations indicated that, as in the bulk liquid case,[3] He^3 was extremely difficult to remove by evaporation from the condensed phase at temperatures below the lambda-point; above this temperature, the distributions between gas and condensed phase were normal. Also, in the measurement of the adsorption isotherms in this work, it was noticed that the observed speed of approach to equilibrium was quite different above and below T_λ.

The early work of Ganz[4] on heat propagation in helium II included some experiments in which a metal tube containing adsorbed film was used for measuring the velocity of transmission of heat. Ganz was apparently able to detect weak heat pulses through the adsorbed He II film, and concluded that thermal energy can be transmitted through the film at quite high velocities.

Finally, the careful measurements of Frederikse[1] on the specific heats of adsorbed He II films of varying thickness showed that the adsorbed layers were undergoing some sort of excitation process which could reasonably be assumed to have some features in common with that which produces the well-known peak in the specific heat curve of the bulk liquid.[5]

It therefore seemed probable that the unsaturated He II film should exhibit some of the unusual features of the behavior of bulk liquid He II. The flow properties seemed the most easily and reliably investigated; a number of experiments were devised, in order to detect, in the unsaturated film, the most striking property of He II, i.e., superfluidity, and, if possible, to evaluate its behavior.
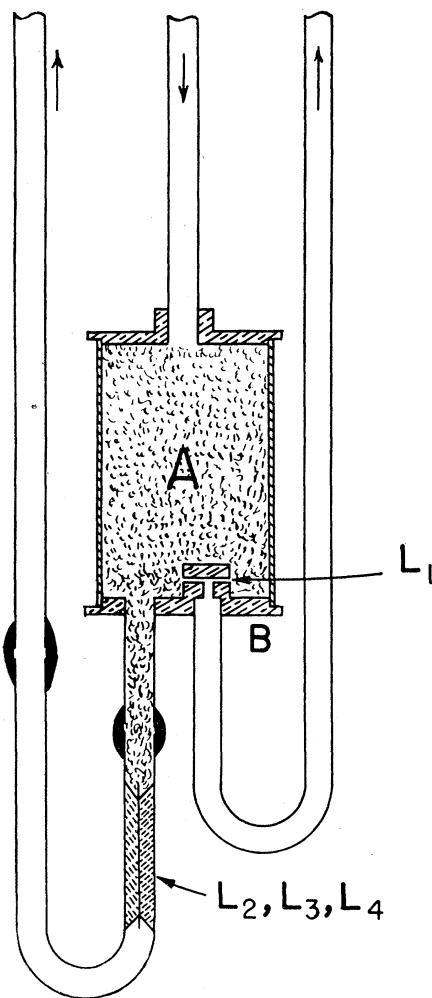
[1] Schaeffer, Smith, and Wendell, J. Am. Chem. Soc. 71, 863 (1949); H. P. R. Frederikse, thesis, Leiden (1950); E. Long and L. Meyer, Phys. Rev. 76, 440 (1949).

[2] See comment by W. Band, Phys. Rev. 76, 441 (1950).
[3] See Taconis, Beenakker, Nier, and Aldrich, Physica 15, 733 (1949).
[4] E. Ganz, Proc. Cambridge Phil. Soc. 36, 127 (1940).
[5] See W. H. Keesom, *Helium* (Elsevier Publishing Company, Amsterdam, 1942), pp. 211–219.
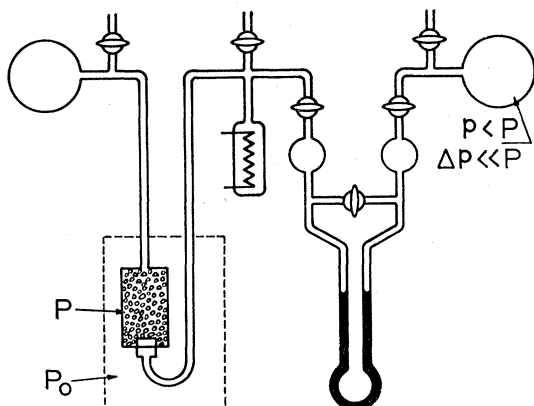
FIG. 2. Measuring system for determining mass flow in adsorbed layers of helium.

In order to measure superflow in the adsorbed film, it is of course necessary to provide a flow system with channels so narrow that ordinary gas flow is negligibly small compared to the film flow itself. Therefore, a technique similar to that used to measure the flow of liquid helium II through narrow channels[6] was adopted, as shown in the apparatus of Fig. 1. A copper chamber, A, containing 75 grams of adsorbent (Fe_2O_3) was sealed at the bottom with a thick stainless steel plate B, through which several narrow channels ("superleaks") L-1, L-2 of varying geometry were connected to the chamber.

Leak L-1 was made by pressing together two optically flat stainless steel circular plates of one-cm diameter, the bottom plate having a central exit channel 0.08-cm diam. Leaks L-2 and L-3 were made by sealing 2.5-cm lengths of 0.013-cm and 0.008-cm diam, respectively, platinum wire into Pyrex glass. Leak, L-4, was similar to L-2 and was mounted in the same manner, but without adsorbent in A. All connecting tubes to the leaks and the adsorbent chamber were 4.8-mm. o.d. ×0.13-mm wall copper-nickel tubing. The whole assembly was immersed directly in the liquid helium bath of the cryostat.

The widths of the leak channels were determined from gas flow measurements under known pressure gradients at 4.2°K. They varied from 1 to 9×10^{-5} cm. The calculation of the channel widths neglected the fact that one dimension of the channels is smaller than the mean free path of the gas, but not the others, a case which is between "Knudsen" gas flow and ordinary viscous flow, and which seems not to have treated at the present time. With channel widths of these dimensions. it seemed that the gas flow would be sufficiently small for the purposes of the experiment.

The adsorption chamber and superleaks were connected to a reservoir and measuring systems, as shown in the schematic diagram of Fig. 2.

The measurements were carried out in two ways. The adsorption chamber was loaded with a constant pressure P of helium gas, always lower than the bath pressure P_0 at temperature T. P/P_0 represents the saturation, and, at any given temperature T, is a measure of the number of adsorbed layers, provided of course that the adsorption isotherms are known.

In method I, at temperature T and saturation P/P_0 in the adsorption chamber, high vacuum was initially pumped on the exit side of the superleak being investigated, then the stopcock leading to the vacuum pump was closed and the pressure rise in a known volume was measured for a given period of time, usually ten minutes, using a Pirani gauge the calibration of which was frequently checked by comparison with a McLeod gauge.

The results of this series of measurements were quite striking. Superfluidity was observed, but the "onset" temperatures for superflow varied from 1.39° at $P/P_0 \sim 0.485$ to 2.04° at $P/P_0 \sim 0.986$, as contrasted to 2.186°K for the start of superflow in the bulk liquid case. The results for eleven different saturations are shown in Fig. 3, in which the flow rate in cc(STP)/min is plotted against the temperature. The number of adsorbed layers varies from ~ 2 at 0.485 to ~ 18 at 0.986.[7] All data shown in Fig. 3 were taken using leak L-2. It will be noted that for each saturation, the onset of superflow is quite sharp, about 0.001°; these onset
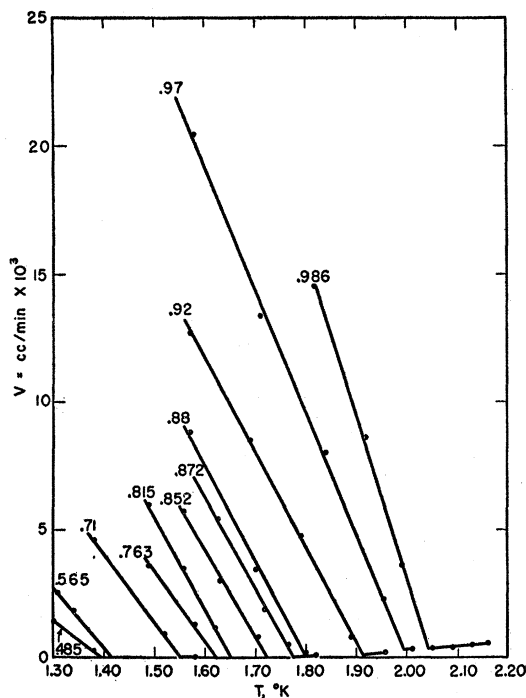

FIG. 3. Flow rate through superleaks as a function of temperature for different saturations.

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[6] See Giauque, Stout, and Barieau, J. Am. Chem. Soc. **61**, 654 (1939); and Osborne, Weinstock, and Abraham, Phys. Rev. **75**, 988 (1949).

[7] As determined from unpublished adsorption isotherms of A. J. Strauss, this laboratory, using the same adsorbent as in these experiments.

temperatures were very reproducible. All the leaks gave the same variation of onset temperature with saturation. Since the leaks must have differed greatly in detailed geometry, it is concluded that these onset temperatures are therefore independent of geometry, for the range of channel sizes used in the experiment. The only determining factors seem to be the number of adsorbed layers, the temperature, and possibly the pumping speed at the exit of the leak.

The fact that in this experiment superflow starts at a temperature which is evidently determined by the number of adsorbed layers is, at the present time, unexplained. However, there seems to be no apparent relationship to the fundamental properties of the film itself, as shown by the experiments of method II.*

In method II, it was reasoned that high vacuum on the exit of the leak would reduce the film thickness near the exit to less than a monolayer. Since the first monolayer of adsorbed helium is so dense that it behaves rather like a solid, it must be considered as immobile. So long as high vacuum is maintained at the exit, film flow is therefore only possible because of a lack of equilibrium between film and vapor which allows the surface of the leak, at least temporarily, to be covered with more layers than correspond to the pressure in the gas phase under the equilibrium conditions given by the adsorption isotherm. This evidently cannot occur until, at some lower temperature, the mobility becomes sufficiently high for the film flow to overcome the pumping rate, permitting the film to flow into the larger connecting tube and evaporate there, rather than in the narrow channel itself.

Therefore, an alternative measuring system was used, as shown in Fig. 2. Instead of initial high vacuum at the leak exit, helium gas was admitted to a pressure p, such that $p<P$, however, $\Delta p \ll P$. Consequently, at least one statistical monolayer was present at all times, and usually the whole leak was covered by practically the same number of layers throughout.

The flow was investigated under these conditions, by balancing the initial pressure p through an oil manometer M against a buffer volume of large capacity, also at p, initially. Thus, measurements of the oil manometer heights as a function of time provide the necessary data for rate of flow through the leak under conditions of essentially constant Δp. The pressure readings were made with a Wild precision cathetometer.

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* *Note added in proof:* However, new evidence has cast doubt on the arguments given to explain the different results of Method I and Method II. Experiments are now being carried out in this laboratory on the heat transport of unsaturated He-II films, using an apparatus similar in principle to that of Bowers, Brewer, and Mendelssohn (Proc. Int. Conference on Low Temperature Physics, Oxford, 1951, p. 75). At any given saturation P/P_0, the contribution of the adsorbed film to the heat transport appears sharply at a temperature which coincides with the onset temperature of Method I, Fig. 3. Since the gradients of pressure and temperature in the heat transport experiment are very small, the explanation of onset temperatures given above cannot be applied to this case. The measurements are being continued; a more detailed report will be submitted to this journal.

In this manner, flow measurements were made over a wide range of saturations and temperatures. Quite different results from those of method I were obtained; for all saturations above $P/P_0=0.15$ ($\sim 1\frac{1}{2}$ statistical layers) superflow was observed at all temperatures below the lambda-temperature of the bulk liquid.

The superflow observed in method II was extremely sensitive to slight variations of the bath temperature. A normal rate of flow from the adsorption vessel to the measuring system was either greatly increased or even reversed by raising or lowering the bath temperature by a few ten-thousandths of a degree.[8]

This dependence of the flow rate and direction of flow on rapid temperature changes was most pronounced with leak L-1, which permitted the highest flow rate, but was also observed with all the other leaks. The magnitude of the effect was greatest at the highest saturations and the higher temperatures in the He II region. No effect was observed below $P/P_0 \sim 0.15$. Furthermore the magnitude was greatest with the smallest values of Δp across the leak; for values of Δp greater than about 10-mm oil, the effect was almost insensitive to Δp, until, with initial high vacuum at the leak exit, the effect disappeared completely.

It was realized that the relatively high thermal capacities of the adsorbent vessel A and the leak assemblies L-1 and L-2 did not permit the system to follow rapid changes of temperature; thus, the system was unable to stay in phase with fluctuations of the bath temperature, so that a temperature gradient was set up across the leak. This, though representing a nonsteady state, is just the condition for thermomechanical effects to occur in the film. Qualitatively, the observed flow behavior was quite analogous to the fountain effect in bulk-liquid helium II.

It was at first thought[8] that the large effects here observed were of about the same magnitude and significance as those of the steady-state measurements on bulk liquid,[9] but later considerations[10] have shown that the thermomechanical effect in adsorbed layers can contribute a ΔP in the gas phase for a given ΔT which is only about 10 percent of the vapor pressure change, whereas in bulk-liquid helium the hydrostatic head resulting from the fountain effect is *ca* ten times the vapor pressure change. It is therefore probable that the phenomenon here observed is a rather severe case of nonequilibrium flow under transient temperature gradients. It is, moreover, true that considerable net mass transfer in either direction can be effected by such temperature gradients in the experiments herein described on the unsaturated film.

Cooling Experiments

Following these studies, it seemed desirable to investigate the flow under more easily controlled and de-

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[8] See E. Long and L. Meyer, Phys. Rev. **79**, 1031 (1950) for a more detailed description.

[9] See L. Meyer and J. H. Mellink, Physica **13**, 197 (1947).

[10] L. Meyer and E. Long, Phys. Rev. **84**, 551 (1951).

finable gradients of both pressure and temperature. For this purpose, the apparatus shown in Fig. 4 was used. An adsorbent chamber A, containing 25 grams of Fe_2O_3, was connected by a 2.5-cm length of thin-walled stainless-steel capillary L, 1.5-mm i.d., to a much smaller chamber B, containing 3.5 grams of Fe_2O_3. The connecting tube was tightly packed with Fe_2O_3 powder, thus constituting an effective superleak, of channel size ca the same as the previous leaks, but of much greater flow capacity. Chambers A and B were connected to the external measuring systems by the stainless steel capillaries C-1 and C-2, of 1.5-mm i.d., which were thermally insulated from the bath by enclosure in the pumping lead P. The apparatus was provided with vacuum insulation by means of the container D, which was sealed to chamber A as shown, so that A was always in direct contact with the bath, whereas chamber B and the superleak L were insulated by high vacuum, as were the connecting leads C-1 and C-2. This arrangement eliminated any effect of accidental fluctuations of the bath temperature on the flow rate.

Carbon thermometers Th-1 and Th-2 were arranged in good thermal contact with chambers A and B, respectively, and a heater H was wound around B. Chambers A and B were of copper, and thus known temperature gradients could be set up along the superleak L.

The capillaries C-1 and C-2 were connected to a system of oil manometers, arranged so that the pressures in each chamber were read independently, and the pressure difference between A and B could be measured directly.

A typical cooling experiment was carried out as follows: With the cryostat bath and whole assembly initially at 2.08°K, chamber A was filled with helium to $P/P_0 = 0.74$ ($\sim$3 layers), and chamber B to P/P_0 0.45 ($\sim$2 layers). Then, by means of heater H chamber B was heated to 2.5°; the system was held with A at 2.08° and B at 2.5° until a steady state was attained. Under these conditions the pressure in B was 90 percent of that in A, but the number of adsorbed layers was of course lower. Then the heater was turned off, and with chamber A still at 2.08°, readings of the pressure in A, the temperature of A, the pressure in B, and the temperature of B were taken as a function of time. Over a period of about one hour, B cooled from 2.5° to 2.12°.

Without superflow, the rate of fall of the pressure in B would be approximately logarithmic, following the temperature of B. However, if superflow starts at any given temperature, film will flow from A into B, and a break in the $\log P_B$ vs time curve should appear. This does happen, as is shown in Fig. 5, in which $\log P_B$ and T_B are plotted against time. There is a distinct break at 27 minutes, at which time the temperature of chamber B was 2.19±0.01°K, as read from the time-temperature curve.

A number of these cooling experiments, with different saturations ranging from $P/P_0 \sim$0.40 to $P/P_0 \sim$0.85, and and with varying initial temperatures in chamber B
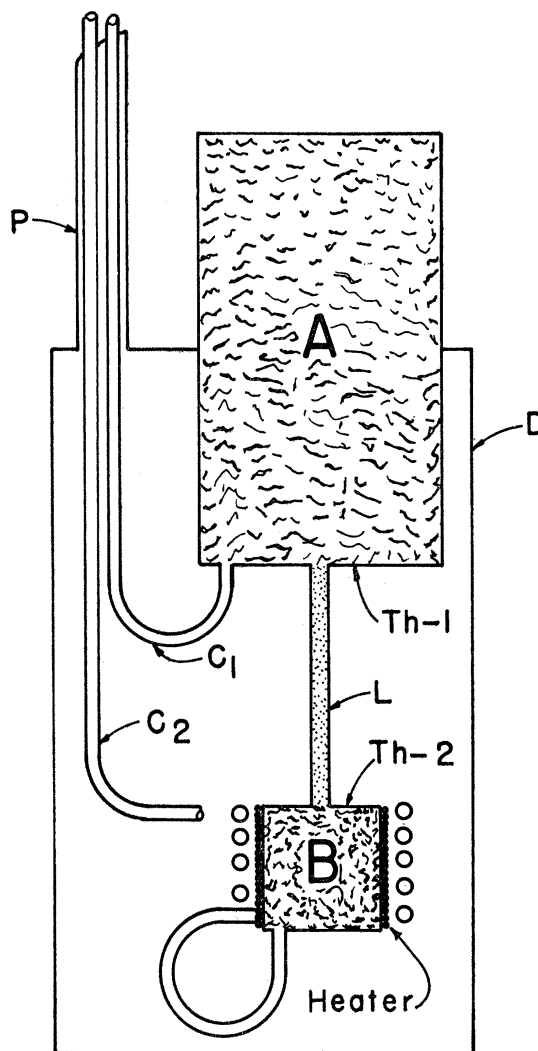

FIG. 4. Apparatus for measuring mass flow in adsorbed layers of helium resulting from temperature gradients.

gave the same result, though not as accurately at the lower saturations. Thus, superfluidity is again seen to start at the normal lambda-point, in agreement with the flow measurements of method II, described previously.

These measurements do not exclude the possibility of the superflow starting at temperatures a few thousandths of a degree above the normal λ-point for the following reasons: (1) It is extremely difficult to perform measurements immediately above the normal λ-temperature. Below T_λ the temperature in the bath is completely homogeneous because of the high heat conductivity of He II. Above T_λ however, the temperature in the lower parts of the bath—where the apparatus usually is situated—is higher than on the top because the liquid is boiling under the hydrostatic pressure head of the bath itself. This amounts to about 0.001° per cm liquid helium. Even with a good stirrer
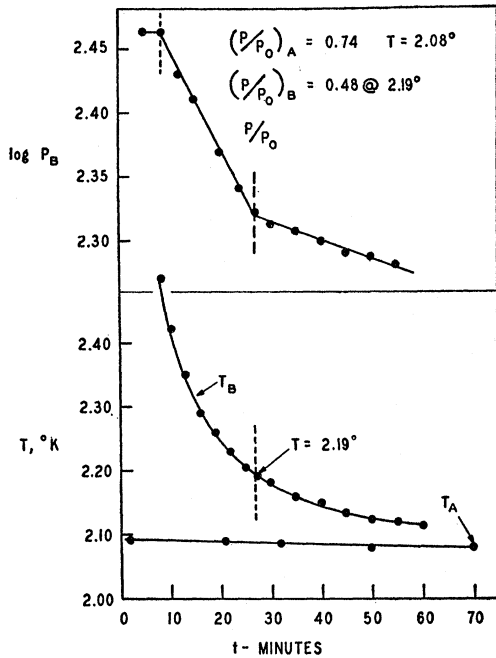
FIG. 5. Changes of pressure and temperature as a function of time in the apparatus of Fig. 4.

it is almost impossible to avoid a jump of some thousandths of a degree in the lower parts of the cryostat when passing T_λ.

(2) It is known from the flow measurements performed with the film in contact with saturated vapor (the so-called Rollin film) that the critical velocity up to which superfluidity occurs decreases rapidly on approching the λ-point. It is therefore quite possible that the real onset of superfluidity in the case of surface layers in equilibrium with unsaturated vapor occurs at a slightly higher temperature than T_λ, and its effects only reach the threshold of our observations below T_λ.

Possibility of Capillary Condensation

Several arguments can be applied to show that capillary condensation cannot be responsible for these flow results: (1) The adsorption isotherms measured on the adsorbent used in these experiments[11] are typical of multi-layer adsorption, and show no sign of capillary condensation.[12] (2) Capillary condensation, if present, would actually lead to entirely different results. Assume that the equilibrium pressure over the adsorbent is not reduced by adsorption, but by capillary condensation; then the well-known Kelvin relation for the vapor pressure over curved surfaces can be applied:

$$RT \log(P/P_0) = 2\gamma V/r, \qquad (1)$$

where γ is the surface tension, V the molar volume of

[11] See reference 1, and unpublished data of A. J. Strauss, this laboratory.
[12] See H. Brunauer, *The Adsorption of Gases and Vapors* (Princeton University Press, Princeton, 1945), where the two types of isotherms are discussed in detail.

the liquid, and r is the radius of curvature, i.e., the radius of the capillary in which condensation occurs. This yields, for 60 percent saturation and 2.18°K, $r \sim 10^{-7}$ cm. In a capillary of this size, the condensed liquid would be under a pressure of *ca* 3 atmospheres; the corresponding λ-temperature is about 0.04° below that of the liquid under vapor pressure,[13] which exceeds by a factor of ten the estimated error of the present experiments on the start of superflow; in this work, no such lowering of the λ-temperature has been observed (3) The appearance of superfluidity has been determined dynamically. If the helium is not distributed by more or less uniform adsorption over the whole surface of the superleak and adsorption system, but is confined by capillary condensation to certain very narrow cavities; these cavities must connect in a continuous path in order to permit superflow. It seems difficult to conceive that the system provides for all measured saturations just the right size cavities, interconnected so as to form a continuous path.

It is indeed an open and interesting question whether capillary condensation is ever possible in a He II system, because of the influence of the thermomechanical effect in the small temperature gradients which are inevitably present.

Relationship to Thermodynamic Data

Aside from the adsorption isotherms, previously discussed, the specific heat measurements of Frederikse[1] are of interest in connection with these flow measure-
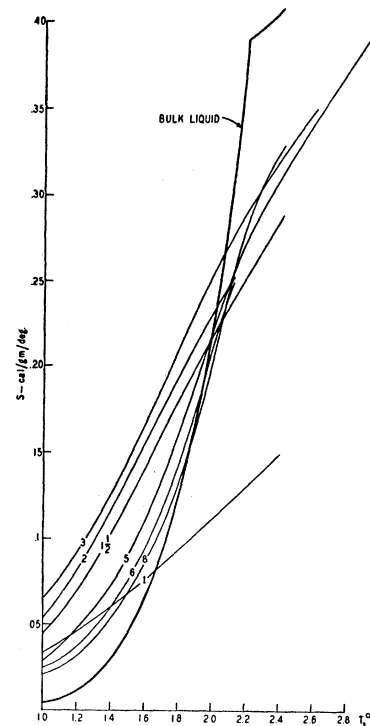

FIG. 6. Entropy of adsorbed layers of helium.

[13] See reference 5, p. 256.

ments. Frederikse found that the maximum in the specific heat-temperature curve, which for bulk liquid helium coincides with the temperature at which superflow appears, namely T_λ, appears also in adsorbed layers, but is broadened and moves to lower temperatures the thinner the coverage, i.e., the lower the saturation. For a coverage of $1\frac{1}{2}$ statistical layers, the specific heat maximum occurs at 1.45°K, whereas the onset of superflow at this coverage is at 2.19°K, the λ-point of the bulk liquid.

These data are not necessarily inconsistent, for it is thermodynamically not required, and even improbable, that the specific heat maxima define the highest temperatures at which the special properties of He II appear (they were indeed not so identified by Frederikse).

It is known that the entropy of adsorbed He is higher than that of the bulk liquid below 2.19°K,[1] as contrasted to the usual case (including He I) for which adsorbed layers possess an entropy lower than that of bulk liquid.[14] An estimate of these entropy relationships

is shown in Fig. 6, in which the entropy of bulk liquid He is compared with that of the unsaturated films as computed by the present authors from the specific heat data of Frederikse.[15] It is seen that the entropy-temperature curves of the adsorbed layers do not show the breaks or kinks which appear in first or second order transitions; the specific heat maxima appear here only as points of inflection. The form of these curves can probably be explained as the result of the competition between two processes: (1) The He II phenomenon, dominant below T_λ (2.186°K), and (2) the ordering process in space, because of the usual van der Waals' forces responsible for adsorption, dominant above T_λ. Thus a sigmoid form of the entropy-temperature curve is produced, and the occurrence of superfluidity in the films at temperatures higher than those of the specific heat maxima is not surprising.

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[14] Compare C. Kemball, *Advances in Catalysis* (Academic Press, New York, 1950), Volume II, p. 233.

[15] For this calculation it was necessary to extrapolate the specific heat data to 0°K, thus introducing a relatively serious error in the absolute values of S; this, however, does not affect the qualitative features of Fig. 1, since the contribution to the total entropy in the extrapolated region is comparatively small.

Phase Transitions in Adsorbed Films

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A thermodynamic treatment of first- and second-order transitions in adsorbed layers is given. The results are compared with the experimental evidence for the melting of argon and the transition He I—He II in adsorbed layers.

A THERMODYNAMIC treatment of transitions for the case in which a condensed phase does not exist in bulk but as adsorbed layers is of interest, since experimental data have recently become available for two examples of such systems: 1. The transition He I— He II (λ-transition).[1-3] 2. The melting point of argon.[4] In the following the effect of surface energies on the melting process (as an example of a first-order transition) and the λ-transition (as an example of a second-order transition) will be treated thermodynamically.

First, consider the case of a first-order transition in a one-component system. From the equality of the chemical potentials in phases 1 and 2 (solid and liquid, respectively) we have, neglecting surface energies, the well-known Clapeyron equation,

$$d\mu_1 = -S_1 dT + V_1 dP = d\mu_2 = -S_2 dT + V_2 dP, \quad (1a)$$

$$(dP/dT)_{equ} = (S_2 - S_1)/(V_2 - V_1), \quad (1b)$$

where S is the molar entropy, V the molar volume, T the temperature, and P the pressure.

If the surface effects cannot be neglected—as in adsorbed layers—a surface energy term must be added to (1a):

$$d\mu_1 = -S_1 dT + V_1 dP - A_1 d\gamma = d\mu_2$$
$$= -S_2 dT + V_2 dP - A_2 d\gamma. \quad (2a)$$

where A is the surface area per mole adsorbed and γ the surface tension.[5] Equation (1b) is changed to,[6]

$$(dP/dT)_{equ} = (S_2 - S_1)/(V_2 - V_1)$$
$$+ (A_2 - A_1)/(V_2 - V_1)(d\gamma/dT)_{equ}. \quad (2b)$$

However, this equation is not directly useful, since $(d\gamma/dT)_{equ}$ is not easily evaluated from experimental data. The surface tension γ is not an independent variable; for a given adsorbent and a given surface

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[1] H. P. R. Frederikse, Physica, 15, 860 (1949), thesis, Leiden, 1950.
[2] E. Long and L. Meyer, Phys. Rev. 76, 440 (1949); Phys. Rev. 79, 1031 (1950).
[3] S. V. R. Mastrangelo, J. Chem. Phys. 18, 846 (1950).
[4] J. A. Morrison and N. E. Drain, J. Chem. Phys. 19, 1063 (1950).

[5] Compare E. A. Guggenheim, *Thermodynamics* (Amsterdam-New York, 1949), pp. 38–39.
[6] For adsorbed films of even a one component system, S, V, and A are not purely extensive properties, but should be treated as partial molal quantities. As there is no ambiguity in the present case, special notation has been omitted.