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.

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Phase Transitions in Adsorbed Films

LOTHAR MEYER AND EARL LONG
Institute for the Study of Metals, University of Chicago, Chicago, Illinois

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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,

$$d\mu_1 = -S_1dT + V_1dP = d\mu_2 = -S_2dT + V_2dP, \qquad (1a)$$

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

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):

$$\begin{aligned} d\mu_1 = -S_1dT + V_1dP - A_1d\gamma &= d\mu_2 \\ &= -S_2dT + V_2dP - A_2d\gamma. \qquad (2a) \end{aligned}$$

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

$$\begin{aligned} (dP/dT)_{\text{equ}} = {} & (S_2 - S_1)/(V_2 - V_1) \\ & + (A_2 - A_1)/(V_2 - V_1)(d\gamma/dT)_{\text{equ}}. \qquad (2b) \end{aligned}$$

However, this equation is not directly useful, since $(d\gamma/dT)_{\text{equ}}$ 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.

area, P and T uniquely determine the amount adsorbed per unit area $(1/A)$ and herewith γ. The equation which enables us to replace the surface tension term in (2b) is supplied by the condition that an adsorbed phase is in equilibrium with the vapor,

$$d\mu_a = -S_a dT + V_a dP - A d\gamma = d\mu_g = -S_g dT + V_g dP, \quad \text{(3a)}$$

where the subscripts a and g denote the adsorbed phase and gas phase, respectively; or, neglecting the volume of the adsorbed phase with respect to that of the gas,[7]

$$-A d\gamma = (S_a - S_g)dT + V_g dP. \quad \text{(3b)}$$

Also,

$$(d\gamma/dT)_{\text{equ}} = (\partial\gamma/\partial T)_P + (\partial\gamma/\partial P)_T (dP/dT)_{\text{equ}}, \quad \text{(4)}$$

and from Eq. (3b),

$$(\partial\gamma/\partial T)_P = (S_g - S_a)/A \quad \text{(5a)}$$

and[8]

$$(\partial\gamma/\partial P)_T = -V_g/A. \quad \text{(5b)}$$

Substitution of (5a) and (5b) in (4) yields

$$(d\gamma/dT)_{\text{equ}} = (S_g - S_a)/A - V_g/A(dP/dT)_{\text{equ}}. \quad \text{(6)}$$

At equilibrium, not only the total free energy but also the surface free energies themselves must be equal, i.e., γ and therefore, $d\gamma/dT$ are the same for both condensed phases 1 and 2. Then using Eq. (6) for either phase 1 or 2 and inserting into Eq. (2b) leads to[9]

$$(dP/dT)_{\text{equ}} = 1/V_g[S_g + A_1S_2/(A_2 - A_1) - A_2S_1/(A_2 - A_1)]. \quad \text{(7a)}$$

This may be rewritten as[10]

$$RT(d\log P/dT)_{\text{equ}} = S_g + A_1S_2/(A_2 - A_1) - A_2S_1(A_2 - A_1), \quad \text{(7b)}$$

or, if $(A_2 - A_1) \ll A$,

$$RT(d\log P/dT)_{\text{equ}} = S_g + (S_2 - S_1)A/(A_2 - A_1). \quad \text{(7c)}$$

THE MELTING CURVE OF ARGON

Applied to a typical first-order process, such as the melting curve, Eqs. (7) have the following meaning: If the melting curve (the change of melting temperature with pressure) crosses the vapor pressure curve to values of $P < P_0$, then the slope is radically different from that at pressures higher than the vapor pressure P_0 of the bulk phase. This is because at P_0 and lower pressures the two condensed phases are in equilibrium not only with each other, but also with the gas phase, thus introducing the term $1/V_g$ in Eqs. (7).

Since V_g is generally large, $(dP/dT)_{\text{equ}}$ is correspondingly reduced, and the change of melting temperature with pressure is thus greater below P_0 than above. However, comparison of Eqs. (7) and (1b) leads to the conclusion that the sign of $(dP/dT)_{\text{equ}}$ must be the same above and below the vapor pressure curve. The phase stable at higher temperatures must have the higher entropy in adsorbed layers as well as in bulk liquid (or solid), so that $(S_2 - S_1)$ cannot change sign. Also $(A_2 - A_1)$ is of the same sign as $(V_2 - V_1)$, since the spacing of atoms or simple molecules in adsorption is usually very nearly the same as that of the bulk liquid or solid, especially for the case of multi-layer adsorption.[11]

Equation (7c) may be tested by the recent results of Morrison and Drain (reference 4) who measured the specific heat of adsorbed argon in the neighborhood of the melting point.[12] The values used for checking Eq. (7c) were

Number of layers	T_m, °K	p, atmospheres
∞	83.7	0.68
4.3	82.0	0.47
3.5	81.7	0.42
2.3	81.0	0.30

A-liquid was computed from the liquid spacing (4.04A)[13] to be 9.9×10^8 cm^2/mole per layer. A-solid was likewise derived from the solid spacing (3.86A)[14] to be 9.0×10^8 cm^2/mole per layer, assuming as usual that the spacing in the adsorbed layers is the same as in the bulk phase. S_g was calculated from the Sackur-Tetrode equation,

$$S_g = R[(3/2)\log M + (5/2)\log T - \log P - 2.298].$$

From these values Eq. (7c) yields $\Delta T_m/\Delta P = +6$ deg/atmos.[15] The value of $\Delta T/\Delta P$ for the bulk phases above P_0 is $+0.024$ deg/atmos as measured by Bridgman,[16] or as calculated from Eq. (1b), using a heat of fusion of 280 cal/mole and a volume change of 3.5 cm^3/mole (reference 13). This illustrates the strong change in slope of the melting curve on crossing the vapor pressure curve; however, the sign remains unchanged, as already shown by the experimental evidence of Morrison and Drain. The melting process observed by Morrison and Drain does not occur at one single temperature, as in the bulk liquid-solid transition, but is spread over a range of 5°–15°, depending on the thickness of the adsorbed film. For comparison with the calculated melting temperatures we choose the high temperature end of

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[7] See reference 5, Eq. (4-72-3).

[8] Eliminating V_g from (5b) by the ideal gas law leads to

$$\partial\gamma = -RT\partial\log P,$$

the familiar form of Gibb's adsorption isotherm.

[9] Equation (7a) can be derived directly from Eq. (6) without the use of Eq. (2b) by the condition that $(d\gamma/dT)_{\text{equ}}$ must be the same for phases 1 and 2.

[10] Equation (7b) is equivalent to Eq. (104) in Terell L. Hill, J. Chem. Phys. **17**, 520 (1949).

[11] Even in the case of helium (reference 2) only the spacing of the first statistical layer can be markedly different from that of the liquid; the succeeding layers must rapidly approach the liquid spacing.

[12] We are indebted to Dr. J. A. Morrison for communicating to us the adsorption isotherm corresponding to the conditions of the specific heat measurements.

[13] Compare O. K. Rice, J. Chem. Phys. **14**, 324 (1946).

[14] Compare O. K. Rice, J. Chem. Phys. **14**, 321 (1946).

[15] In using the values of A_{liquid} and A_{solid} given above in Eq. (7c), it is assumed that even in multilayer adsorption the numbers of statistical layers for phase 1 and 2 in equilibrium are essentially the same, and that the spacing of the atoms determines the area per mole.

[16] P. W. Bridgman, Proc. Am. Acad. Sci. **70**, 1 (1935).

the specific heat anomaly (Fig. 2, reference 4) instead of the temperature of the maximum, for the following reason: An adsorbed phase is—because of the field of force of the wall—a highly inhomogenous phase. The temperature which corresponds to the thermodynamic calculation of the melting point is the highest temperature at which the solid phase appears in equilibrium with the liquid phase, just as the melting point of a solution is the highest temperature at which the solid phase appears. In adsorbed layers, the freezing is not completed at this temperature, presumably because the layers nearer to the wall must form more and more distorted lattices because of the mismatch with the substrate; in the case of argon this would reduce the melting temperature. Under this assumption, we obtained the values of T_m tabulated above, as read from Fig. 2 of reference 4. The experimental value of $\Delta T_m/\Delta P$ is 6–8 deg/atmosphere, in excellent agreement with the value calculated from Eq. (7c); considering the approximation necessary to evaluate the quantities of (7c), not much more than an order of magnitude agreement could be expected.

THE λ-TRANSITION IN HELIUM

The transition He I—He II is second order; instead of Eq. (2b) we must use the equivalent of the Ehrenfest equations:

$$\left(\frac{dp}{dT}\right)_\lambda=\frac{\dfrac{\partial S_2}{\partial T}-\dfrac{\partial S_1}{\partial T}}{\dfrac{\partial V_2}{\partial T}-\dfrac{\partial V_1}{\partial T}}+\frac{\dfrac{\partial A_2}{\partial T}-\dfrac{\partial A_1}{\partial T}}{\dfrac{\partial V_2}{\partial T}-\dfrac{\partial V_1}{\partial T}}\left(\frac{d\gamma}{dT}\right)_\lambda$$

$$=\frac{\dfrac{\partial S_2}{\partial P}-\dfrac{\partial S_1}{\partial P}}{\dfrac{\partial V_2}{\partial P}-\dfrac{\partial V_1}{\partial P}}+\frac{\dfrac{\partial A_2}{\partial P}-\dfrac{\partial A_1}{\partial P}}{\dfrac{\partial V_2}{\partial P}-\dfrac{\partial V_1}{\partial P}}\left(\frac{d\gamma}{dT}\right)_\lambda. \quad (8)$$

From the same argument, which leads from (2b) to (7) we derive from (8)

$$\left(\frac{dP}{dT}\right)_\lambda=\frac{1}{V_g}\left\{S_g-S_a+A\frac{\partial S_2/\partial T-\partial S_1/\partial T}{\partial A_2/\partial T-\partial A_1/\partial T}\right\}$$

$$=\frac{1}{V_g}\left\{S_g-S_a-A\frac{\partial V_2/\partial T-\partial V_1/\partial T}{\partial A_2/\partial P-\partial A_1/\partial P}\right\}. \quad (9)$$

It would be of interest to apply Eq. (9) to the data of Frederikse (reference 1) who measured the specific heat and adsorption isotherms of unsaturated helium films in the region of the transition He I—He II. However—even though the data represent a considerable experimental achievement—it seems at present impossible to evaluate with sufficient accuracy the second-order terms in Eq. (9) for comparison with experiment as was done for Eq. (7). But the qualitative features remain the same, as may be seen from an examination of (9): The slope of the λ-curve must change strongly on passing the vapor pressure curve to values $P<P_0$, but the sign should not change as long as the second order terms in Eq. (9) are dominant.[17] Thus since $\Delta T/\Delta P$ is negative above P_0, the transition in adsorbed films is expected to occur at temperatures above the λ-temperature of the bulk liquid. The effect should be very small, since the vapor pressure of the liquid at the λ-point is only 0.05 atmosphere and the total available pressure range 0.04 atmos.

The data of Frederikse show that the specific heat anomaly resulting from the He I—He II transition in adsorbed layers is smeared out in a manner similar to the melting point of argon. If again the first appearance of an anomalous thermal effect on cooling the system is chosen as the temperature characteristic for the transition, the specific heat curves are in agreement with these conclusions; the anomalous rise in specific heat always occurs between 2.2° and 2.3°K.

The superfluid properties of bulk liquid helium disappear above the λ-point. The fact that superflow is observed in unsaturated films at all temperatures below the normal λ-temperature[18] is another confirmation of these considerations, showing that the transition temperature in these films is practically the same as T_λ.[19]

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[17] An order of magnitude estimate can be derived under the following admittedly rather crude assumptions which might be somewhat justified for more than several statistical layers and a saturation P/P_0 just slightly smaller than 1: The value of $(\partial S_2/\partial T)-(\partial S_1/\partial T)=\Delta c/T$ (c being the specific heat) equals that of the bulk liquid. The spacing in the adsorbed layers is the same as in the bulk liquid so that $(1/A)dA/dT=\frac{2}{3}(1/V)dV/dT$. Using $\Delta c=-7.6$ cal/mole deg and $\Delta(1/V)(dV/dT)=0.065$ deg^{-1} as given by Keesom [see W. H. Keesom, *Helium* (Elsevier Publishing Company, Amsterdam, 1942), p. 256] the third term inside the brackets of (9) is about 160 cal/mole deg, compared with 10 cal/mole deg for S_g-S_a, the entropy of adsorption. These assumptions lead to $(\Delta T/\Delta P)=-0.45$ deg/atmosphere compared with -0.012 deg/atmosphere above P_0.

[18] See reference 2 and E. Long and L. Meyer, Phys. Rev. **85**, 1030 (1952) [preceding article].

[19] Mastrangelo (reference 3) has recently discussed the specific heat maxima of unsaturated helium films and has attempted a correlation of these maxima with the shift of the λ-temperature in bulk liquid with pressure. It should therefore be emphasized that the pressure entering thermodynamic relationships concerning unsaturated films is the pressure of the gas phase in equilibrium with the film, which is always smaller than P_0, the vapor pressure. The pressures which Mastrangelo assumes in his treatment have no relationship to the thermodynamic pressure.