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## Pressure Coefficient and Compressibility of Liquid $He^4$ Very Close to the $\lambda$ Curve*

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Measurements of the pressure coefficient $\beta_V=(\partial p/\partial T)_V$ and the compressibility $\kappa_T=-(1/V)(\partial V/\partial p)_T$ in the immediate vicinity of the point $p_\lambda=13.04$ atm, $V_\lambda=24.20$ cm$^3$/mole, $T_\lambda=2.023$°K are described. For $\beta_V$ the smallest increments were $\Delta T\simeq 2\times10^{-5}$°K and for $\kappa_T$ they were $\Delta p\simeq 1\times10^{-3}$ atm corresponding to $\Delta V/V\simeq 8\times10^{-6}$. From about $2\times10^{-2}$°K to within $10^{-5}$°K of $T_\lambda$, $\beta_V$ is given by relations

$$\beta_{V=V_\lambda}=3.5+3.4\log_{10}|T-T_\lambda| \quad \text{(He I)},$$
$$\beta_{V=V_\lambda}=-6.0+2.3\log_{10}|T-T_\lambda| \quad \text{(He II)}.$$

$\kappa_T$, from $10^{-2}$ to $10^{-3}$ atm of $p_\lambda$, may be represented by equations

$$\kappa_T=0.0079-0.02(p-p_\lambda)-1.5(T-T_\lambda) \quad \text{(He I)},$$
$$\kappa_T=0.0089+0.11(p-p_\lambda)+8.4(T-T_\lambda) \quad \text{(He II)}.$$

In these relations $T$ is expressed in °K, $p$ in atm, $\beta_V$ in atm/°K, and $\kappa_T$ in atm$^{-1}$. Close to the $\lambda$ curve $\beta_V$ is thus a linear function of $\log|T-T_\lambda|$ and $\kappa_T$ has a discontinuity at the transition point amounting to about 10% of its value. The results are discussed on the basis of thermodynamic equations derived recently by Buckingham and Fairbank.

### I. INTRODUCTION

NEAR the $\lambda$ curve the properties of liquid $He^4$ change rapidly. Consequently, for studying the thermodynamics of the transition He I $\rightleftarrows$ He II measurements have to be made very close to the $\lambda$ curve with exceedingly small increments of the variables. Only thus can useful information be obtained about the $\lambda$ transition itself. In this paper, measurements of the pressure coefficient $\beta_V=(\partial p/\partial T)_V$ and the compressibility $\kappa_T=-(1/V)(\partial V/\partial p)_T$ in the immediate vicinity of the point $p_\lambda=13.04$ atm, $V_\lambda=24.20$ cm$^3$/mole, $T_\lambda=2.023$°K ($p_\lambda$, $V_\lambda$, and $T_\lambda$ always refer to these values of $p$, $V$, and $T$) are described. The point $(p_\lambda,V_\lambda,T_\lambda)$ is on the $\lambda$ curve.[1] For $\beta_V$ the smallest increments were $\Delta T\simeq 2\times10^{-5}$°K and for $\kappa_T$ they were $\Delta p\simeq 1\times10^{-3}$ atm corresponding to $\Delta V/V\simeq 8\times10^{-6}$. Measurements of the pressure coefficient were thus done with almost two orders of magnitude smaller temperature increments and two orders of magnitude closer to the $\lambda$ curve than in the previous work of Lounasmaa and Kaunisto.[1] A similar improvement was obtained for $\kappa_T$ as compared with the experiments of Grilly and Mills.[2] The present results indicate that close to the $\lambda$ curve $\beta_V$ is a linear function of $\log|T-T_\lambda|$ and that $\kappa_T$ has a discontinuity at the transition point.

### II. EXPERIMENTAL

The apparatus is schematically shown in Fig. 1. Parts not drawn include a vacuum case insulating the piezometer ($G$) from the main helium bath, and a helium and a nitrogen Dewar. ($G$) was first cooled down to 4.2°K with the help of exchange gas which was then removed. Next, the temperature of the bath was lowered to 2.2°K by pumping and ($G$) filled approximately to the desired pressure. Simultaneously, liquid helium at 2.2°K was condensed to the upper compartment ($E$).

* Based on work performed, in part, under the auspices of the U. S. Atomic Energy Commission.
† Present address: Wihuri Physical Laboratory, University of Turku, Turku, Finland.
[1] O. V. Lounasmaa and L. Kaunisto, Ann. Acad. Sci. Fennicae: Ser. AVI, No. 59 (1960).
[2] E. R. Grilly and R. L. Mills, Ann. Phys. (N. Y.) **18**, 250 (1962).

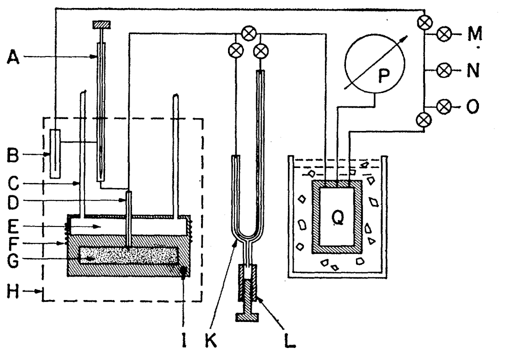


FIG. 1. Schematic drawing of the apparatus. (*A*) needle valve; (*B*) charcoal purifier at 4.2°K; (*C*) pumping and vapor pressure tubes (2) for (*E*); (*D*) tube connecting (*G*) with (*A*) and (*K*); (*F*) heater; (*G*) piezometer packed with thin copper wire for rapid equilibrium (volume 38.77 cm$^3$ at 4°K, height 10 mm to keep hydrostatic pressure differences small); (*H*) dashed lines enclose space at 4.2°K or below; (*I*) germanium thermometer; (*K*) differential oil manometer (left-hand tube: length 40 cm, bore 1.89 mm$^2$; right-hand tube: length 90 cm, bore 1.99 mm$^2$); (*L*) oil reservoir filled with Apiezon *B* oil; (*M*) to He$^4$ supply tank; (*N*) to pump; (*O*) to atmosphere; (*P*) 25-cm dial test gauge calibrated against a dead weight tester; (*Q*) ballast volume (1461 cm$^3$) for balancing the right-hand side of (*K*); ⊗ needle valves.

The bath was then allowed to warm up to 4.2°K and helium in (*G*) brought to the point ($p_\lambda, V_\lambda, T_\lambda$). The temperature in (*G*) was controlled by the heater (*F*) and by pumping on liquid helium in (*E*). Since the temperature could thus be kept constant when desired, the measurements of $\beta_V$ and $\kappa_T$ were done under equilibrium conditions.

For differential measurements of the present type it is very important that the amount of He$^4$ in the dead volumes outside (*G*) remains the same as accurately as possible. The dead volume thus had to be made small and its temperature kept constant. Accordingly, the tube (*D*) connecting (*G*) with the oil manometer (*K*) was a german-silver capillary of 0.1 mm i.d. from (*G*) to the top of the cryostat and then increased to 0.5 mm i.d. Further, this tube was isolated from the helium bath by vacuum and it was kept warm down almost to the top of the vacuum case by soldering it inside a 1-mm copper tube extending to room temperature. (*G*) could not be filled through the long 0.1-mm tube owing to the possibility of blocks caused by tiny amounts of impurities in the He$^4$ gas. A needle valve (*A*), closing in the immediate vicinity of (*G*), was, therefore, constructed for admitting He$^4$ to (*G*). After these precautions, no spurious effects were observed during pressure measurements.

The method of measuring $\beta_V$ was essentially similar to that commonly employed in constant volume gas thermometry. The pressure change produced in (*G*) by a small, known, temperature change was determined with the differential oil manometer (*K*). During these measurements the oil level in the left-hand manometer tube was kept constant within 0.01 mm and pressure changes were read from the right-hand tube with a cathetometer. At each point the temperature was stabilized for about 5 min before a measurement was taken. To the observed pressure differences 21.6% had to be added because of compression of He$^4$ gas in (*Q*) due to movements of oil in the right-hand manometer tube.[3] Including this correction, 1 cm of oil corresponded to $1.008\times10^{-3}$ atm. The temperature of the ice bath around (*Q*) had to remain constant to about 0.001°C during the measurement of one pressure change. This was achieved by using distilled ice and water and by an effective stirring arrangement.

In measuring $\kappa_T$ the molar volume of He$^4$ in (*G*) was changed by raising the oil level gradually in the left-hand manometer tube and thereby pushing more He$^4$ into (*G*). A 1-cm rise corresponded to $\Delta V/V=6.32\times10^{-6}$. The pressure changes in (*G*) were calculated as for $\beta_V$ except that movements of oil in both manometer tubes had to be taken into account. During the measurements of $\kappa_T$ the temperature was kept constant within $0.5\times10^{-6}$°K.

For these experiments it is of utmost importance to determine the point ($p_\lambda, V_\lambda, T_\lambda$) accurately. Starting slightly below $T_\lambda$ and by allowing the temperature in (*G*) to increase slowly the λ point could be located within $0.5\times10^{-6}$°K from a change in the slope of the warming-up curve. The position of oil level in the left-hand manometer tube at the transition could be determined with a precision of 0.3 mm, corresponding to a relative accuracy of $3\times10^{-5}$ atm in the pressure. For temperature measurements an ordinary carbon thermometer was employed at first, but this proved unsuitable owing to an apparent drift of about $5\times10^{-5}$°K/h after cooling down. This drift rate became smaller with time but was still easily detectable after 24 h from the beginning of an experiment. The required stability of $0.5\times10^{-6}$°K was achieved with a Radiation Research Company germanium thermometer (Model CG-1). Its sensitivity was 670 Ω/°K at $T_\lambda$ and its resistance was measured to 0.0003 Ω in a potentiometer circuit (Rubicon No. 2773 double potentiometer). The thermometer was calibrated against the vapor pressure of He$^4$, measured from (*E*), on the $T_{58}$ scale.[4]

All the final measurements (3 runs for $\beta_V$ and 4 runs for $\kappa_T$) were made during a single 9-day experiment. This insured that the bulk quantity of He$^4$ in (*G*) remained constant.

Originally, it was planned to measure also $C_V$, the specific heat at constant volume, very close to ($p_\lambda, V_\lambda, T_\lambda$). The present apparatus, however, proved somewhat unsuitable for this purpose and the experiments were abandoned.

[3] O. V. Lounasmaa, thesis, Oxford, 1958 (unpublished); R. W. Hill and O. V. Lounasmaa, Phil. Trans. Roy. Soc. London **252**, 357 (1960).

[4] F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. **A64**, 1 (1960).

## III. RESULTS

The experimental results on $\beta_V$ are shown in Fig. 2; they cover the temperature range from $10^{-3}$°K to within $10^{-5}$°K of $T_\lambda$. Lounasmaa and Kaunisto[1] have measured $\beta_V$ from $10^{-1}$°K to within $10^{-3}$°K of the transition temperature. One of their experimental runs was made in the vicinity of the point $p_\lambda'=13.02$ atm, $V_\lambda'=24.21$ cm$^3$/mole, $T_\lambda'=2.0214$°K, which is so close to the point $(p_\lambda,V_\lambda,T_\lambda)$ that their results are directly comparable with the present ones. As may be seen from Fig. 2, the agreement is very satisfactory. Together the two sets of data cover a range of about 4 orders of magnitude in $|T-T_\lambda|$ on both sides of $T_\lambda$.

Points in the He I and He II regions separate clearly and, furthermore, on a $\beta_V$ vs $\log|T-T_\lambda|$ plot, from about $2\times10^{-2}$°K to the smallest experimental values of $|T-T_\lambda|$, they fall on two straight lines with equations (along the isochore $V=V_\lambda$)

$$\beta_{V=V_\lambda}=3.5+3.4\log_{10}|T-T_\lambda|, \quad \text{(He I)} \tag{1a}$$

$$\beta_{V=V_\lambda}=-6.0+2.3\log_{10}|T-T_\lambda|, \quad \text{(He II)}, \tag{1b}$$

where $T$ is expressed in °K and $\beta_V$ in atm/°K. These expressions are similar to those used previously for $C_p$ and $\alpha_p=(\partial V/\partial T)_p$ along the saturation vapor pressure curve of He[4],[5–8] except that the two lines are not

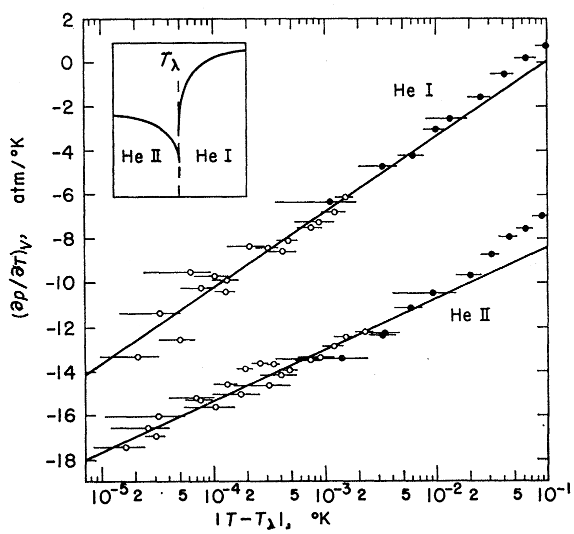


FIG. 2. Results of measurements of $\beta_V=(\partial p/\partial T)_V$ along the isochore $V=V_\lambda(p\simeq13$ atm, $T_\lambda=2.023$°K): ○ present measurements, ● Lounasmaa and Kaunisto.[1] Equations of the straight lines: $\beta_{V=V_\lambda}=3.5+3.4\log_{10}|T-T_\lambda|$ (He I), $\beta_{V=V_\lambda}=-6.0+2.3\log_{10}|T-T_\lambda|$ (He II). Horizontal lines extending through each point give the temperature increment used in determining $\beta_V$. The behavior of the pressure coefficient near $T_\lambda$ is shown on a linear plot in the upper left corner.

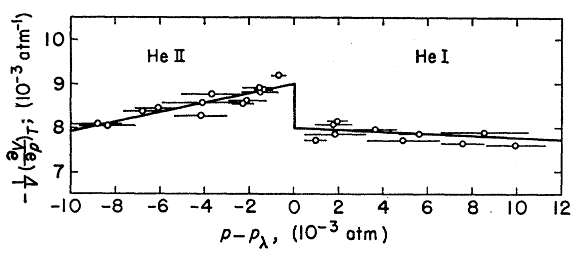


FIG. 3. Results of measurements of $\kappa_T=-(1/V)(\partial V/\partial p)_T$ along the isotherm $T=T_\lambda$ ($p\simeq13$ atm, $T_\lambda=2.023$°K). Equations of straight lines: $\kappa_{T=T_\lambda}=0.0079-0.02(p-p_\lambda)$ (He I), $\kappa_{T=T_\lambda}=0.0089+0.11(p-p_\lambda)$ (He II). Horizontal lines extending through each point give the pressure increment used in determining $\kappa_T$.

parallel to each other. In fact, if Eqs. (1) are extrapolated towards $T_\lambda$, the lines cross at $2\times10^{-9}$°K, where $\beta_V=-26$ atm/°K. Further, at $T=T_\lambda$ the relations give $\beta_V=-\infty$. This, however, is impossible since the pressure coefficient cannot have a larger absolute value than the slope of the λ curve,[1,9] which at $(p_\lambda,V_\lambda,T_\lambda)$ is $(dp/dT)_\lambda=-76$ atm/°K.[1] Equations (1) thus have to break down very close to $T_\lambda$. [According to (1a), $\beta_V=-76$ atm/°K at $|T-T_\lambda|=10^{-23}$°K.]

The scatter of points in Fig. 2 gives a good idea of the relative accuracy of these measurements. Their absolute precision, particularly in view of the good agreement between the present results and the earlier work of Lounasmaa and Kaunisto,[1] is estimated as 2% at $T-T_\lambda=\pm10^{-3}$°K.

Results of measurements of $\kappa_T$, covering a range from $10^{-2}$ to within $10^{-3}$ atm of $p_\lambda$, are shown in Fig. 3. Unfortunately, it was impossible to investigate a wider pressure range in our apparatus. The results show that $\kappa_T$ has a discontinuity at the λ point amounting to about 10% of its magnitude. Closer than $10^{-2}$ atm to $p_\lambda$ and along the isotherm $T=T_\lambda$, $\kappa_T$ is, within the experimental accuracy, a linear function of $p$; thus

$$\kappa_{T=T_\lambda}=0.0079-0.02(p-p_\lambda), \quad \text{(He I)} \tag{2a}$$

$$\kappa_{T=T_\lambda}=0.0089+0.11(p-p_\lambda), \quad \text{(He II)}. \tag{2b}$$

In the immediate vicinity of the point $(p_\lambda,V_\lambda,T_\lambda)$ $\kappa_T$ only depends on the distance from the λ curve and we may thus write $p-p_\lambda=-(dp/dT)_\lambda(T-T_\lambda)$. By combining this result with Eqs. (2), we get for $\kappa_T$ as a function of $p$ and $T$

$$\kappa_T=0.0079-0.02(p-p_\lambda)-1.5(T-T_\lambda), \quad \text{(He I)} \tag{3a}$$

$$\kappa_T=0.0089+0.11(p-p_\lambda)+8.4(T-T_\lambda), \quad \text{(He II)} \tag{3b}$$

where $T$ is in °K, $p$ in atm, and $\kappa_T$ in atm$^{-1}$.

The experimental measurements of $\kappa_T$ along the isotherm $T=T_\lambda$ can also be expressed as a function of $V$. One may further write, with the same justification as above, $V-V_\lambda=-(dV/dT)_\lambda\cdot(T-T_\lambda)$, where $(dV/dT)_\lambda=12.9$ cm$^3$/mole °K is the slope of the λ curve in the

[5] W. M. Fairbank, M. J. Buckingham, and C. F. Kellers, *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, August 30, 1957* (University of Wisconsin Press, Madison, Wisconsin, 1958), p. 50.

[6] K. R. Atkins and M. H. Edwards, Phys. Rev. **97**, 1429 (1955).

[7] M. H. Edwards, Can. J. Phys. **36**, 884 (1958).

[8] C. E. Chase, E. Maxwell, and W. E. Millett, Physica **27**, 1129 (1961).

[9] L. Goldstein, Phys. Rev. **122**, 726 (1961).

TABLE I. Comparison of $\beta_V$ (in atm/°K) as calculated from relations (1) and (5).

| $\|T-T_\lambda\|$ (°K) | He I (1) | He I (5) | He II (1) | He II (5) |
|---|---|---|---|---|
| $1\times10^{-5}$ | $-13.6$ | $-8.4$ | $-17.6$ | $-15.7$ |
| $3\times10^{-5}$ | $-12.0$ | $-8.2$ | $-16.5$ | $-14.7$ |
| $1\times10^{-4}$ | $-10.2$ | $-7.4$ | $-15.3$ | $-11.3$ |

$V$, $T$ plane.[1] We thus obtain for $\kappa_T$ as a function of $V$ and $T$

$$\kappa_T=0.0079+0.10(V-V_\lambda)-1.3(T-T_\lambda), \quad \text{(He I)} \quad (4a)$$

$$\kappa_T=0.0089-0.51(V-V_\lambda)+6.6(T-T_\lambda), \quad \text{(He II)} \quad (4b)$$

where $T$ is in °K, $V$ in cm$^3$/mole, and $\kappa_T$ in atm$^{-1}$.

The absolute accuracy of $\kappa_T$ is estimated as 3% at $p-p_\lambda=\pm10^{-2}$ atm; the relative accuracy may be seen from the scatter of points in Fig. 3.

## IV. DISCUSSION

By employing a method due to Buckingham and Fairbank[10] the following relation, valid in the immediate vicinity of the $\lambda$ curve, can be derived for the pressure coefficient:

$$\beta_V=(dp/dT)_\lambda+(dV/dT)_\lambda/\kappa_T V. \quad (5)$$

A few values calculated for $\beta_V$ by using this equation and relations (4) (by putting $V=V_\lambda$) for $\kappa_T$ are compared with directly measured data (1) in Table I. At $10^{-5}$°K the agreement is quite good for He II but less satisfactory for He I. However, not a very close agreement can be expected since $\beta_V$ from (5) is obtained as the difference of two large quantities and thus an error of 3% in $(dp/dT)_\lambda$, $(dV/dT)_\lambda$, or $\kappa_T$ would change the calculated value of $\beta_V$ by about 20%. At distances greater than $10^{-4}$°K from the $\lambda$ curve the agreement rapidly becomes poorer presumably for two reasons. Firstly, (5) is no longer valid to sufficient accuracy. By employing the relation[10,11]

$$\alpha_p=(dV/dT)_\lambda+\kappa_T V(dp/dT)_\lambda \quad (6)$$

to measurements of $\alpha_p$ and $\kappa_T$ along the saturation vapor pressure curve Chase, Maxwell, and Millett[8] found that (6) is valid only at temperatures closer than $10^{-4}$°K to the $\lambda$ point. A similar range of validity may be expected for (5) also. Chase *et al.* further observed that the agreement is better in He II than in He I region. Secondly, the present measurements of $\kappa_T$ cover only 1 order of magnitude in $p-p_\lambda$, and one would thus expect that relations (2–4) might rapidly lose their usefulness at pressures outside $10^{-2}$ atm (corresponding to $10^{-4}$°K) of the transition point. The true temperature dependence of $\kappa_T$ might be rather different from that given in Eqs. (2)–(4) and this would also explain the discrepancies. As an example, in He I region, according to (5), $\beta_V=0$ at $T-T_\lambda=7\times10^{-4}$°K, whereas in reality this only happens at $6\times10^{-2}$°K (Fig. 2). Equation (1a) gives for this temperature $9\times10^{-2}$°K.

Several other relations, suitable for comparing different thermodynamic quantities of He$^4$ near the $\lambda$ curve have been derived by Buckingham and Fairbank.[10] Unfortunately, due to considerable difficulties in making precise measurements close to the transition temperature, very few experimental data are available for such a comparison. Furthermore, most of these investigations have been done under saturation vapor pressure even though measurements in the pure liquid phase are more fundamental. Besides the experiments on $\beta_V$ by Lounasmaa and Kaunisto[1] the present results may only be compared with the $C_V$ data of Lounasmaa and Kojo.[12] This can be done by employing the following relation,[10] valid at the $\lambda$ curve:

$$C_{V,\lambda}=T_\lambda(dS/dT)_\lambda-T_\lambda(dV/dT)_\lambda(dp/dT)_\lambda. \quad (7)$$

The values of $T_\lambda$, $(dV/dT)_\lambda$, and $(dp/dT)_\lambda$ have already been given; $(dS/dT)_\lambda=3.9$ J/mole °K$^2$.[13] We thus get $C_{V,\lambda}=208$ J/mole °K. Experimental data by Lounasmaa and Kojo[12] are about 40 J/mole °K. The smallest temperature increments used in the $C_V$ experiments were about $7\times10^{-3}$°K which explains the discrepancies. For a more meaningful comparison, measurements with at least 2 orders of magnitude smaller temperature increments would be most desirable.

The thermal expansion coefficient $\alpha_p$ can be calculated from (6) or from the general thermodynamic relation $\alpha_p=V\kappa_T\beta_V$. Results by the latter method are probably valid over a wider temperature range than those obtained by using Eq. (6).

Buckingham and Fairbank[10] have derived equations [relations (5)–(7) are examples] for a transition characterized by the absence of a latent heat but at which $C_p$ becomes infinite. Their results show that at such a transition $\alpha_p$ and $\kappa_T$ both become infinite and that $\beta_V=(dp/dT)_\lambda$. $C_V$ will have the finite value given by (7). The present measurements seem to contradict some of these conclusions. Firstly, it seems doubtful (cf. Fig. 2) whether $\beta_V$ can reach the value $-76$ atm/°K at $T=T_\lambda$ when this point is approached from either side. Secondly, there are no indications at all (cf. Fig. 3) that $\kappa_T$ would be tending towards infinity at the $\lambda$ point. However, according to Chase, Maxwell, and Millett[8] one would have to come exceedingly close to the transition curve ($10^{-68}$°K for a 100% increase in $\kappa_T$) before this trend becomes apparent.

Previous measurements of $C_p$ by Fairbank, Buckingham, and Kellers[5] and of $\alpha_p$ by several groups of inves-

[10] M. J. Buckingham and W. M. Fairbank, *Progress in Low-Temperature Physics*, edited by J. C. Gorter (North-Holland Publishing Company, Amsterdam, 1961), Vol. 3, p. 80.

[11] A. B. Pippard, Phil. Mag. 1, 473 (1956).

[12] O. V. Lounasmaa and E. Kojo, Ann. Acad. Sci. Fennicae Ser. AVI, No. 36 (1959).

[13] O. V. Lounasmaa, Cryogenics 1, 212 (1961).

tigators[6–8,14] along the saturation vapor pressure curve indicate that both these quantities have logarithmic-type singularities at the λ point and that they may be represented by equations similar to (1), with the important difference that the two lines corresponding to He I and He II are parallel to each other. Experimental evidence for parallelism is strong in the case of $C_p$ but much less so for $\alpha_p$. It is quite possible, on the basis of results by Chase *et al.*,[8] that the line corresponding to $\alpha_p$ in He II region has a smaller slope than that in He I region, as in the case of $\beta_V$ (cf. Fig. 2). However, there is a basic difference between $C_p$ and $\alpha_p$ on one side and $\beta_V$ on the other: $\beta_V$ has a finite value at the transition point and thus a logarithmic equation (1) cannot be valid right up to $T=T_\lambda$, whereas for $C_p$ and $\alpha_p$ there is no reason, in principle, why this could not be so. When the present measurements are taken into account, the difference in the slopes of the straight lines in Fig. 2 becomes more pronounced than it was according to the observations of Lounasmaa and Kaunisto.[1]

[14] E. C. Kerr and R. D. Taylor, in *Proceedings of the International Conference on Low-Temperature Physics, Toronto, 1960* (University of Toronto Press, Toronto, 1961), p. 538.

Direct measurements of $C_V$ and $\alpha_p$ with very small increments of temperature would provide valuable information about the λ transition and such data could be used, together with the present results, for checking the relations of Buckingham and Fairbank[10] if the experiments were made close to the point $(p_\lambda,V_\lambda,T_\lambda)$. Measurements of $\kappa_T$ should also be extended over a wider pressure range.

When experiments with smaller and smaller temperature increments have been made, the apparent character of the λ transition in liquid $He^4$ has been shifting from one with sharp discontinuities in $C_p$ and $\beta_V$ to one at which these quantities change less drastically, showing that the transition is of milder character than was originally assumed.

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