

Experimental data substituted in the latter equation show that, over the range 50–225 kg/cm², $\Delta\beta$ has a constant value of $\sim 2.5 \times 10^{-5}$ cm²/kg, which is at most 2.5 percent of β_f . At 3555 kg/cm² $\Delta\beta$ is calculated to be 2.8×10^{-6} cm²/kg or 5 percent of β_f . The compressibility coefficient of solid He³ is therefore very similar to that of the fluid along the full range of the melting curve investigated. For Na and K, the data of Bridgman (34) lead to values of 38 and 29 percent, respectively, for $\Delta\beta/\beta_f$ at $P_m = 1$ kg/cm².

C. THERMAL PROPERTIES OF MELTING

At the lower end of the P_m range for He³, the ΔS_m results were combined with the entropy of saturated liquid S_{sat} , measured by Roberts and Sydoriak (35), and the entropy of compression ΔS_{comp} to give the entropy of solid. The values of ΔS_{comp} can be obtained through the formula

$$\Delta S_{\text{comp}} = - \int_{P_{\text{sat}}}^{P_m} \left(\frac{\partial V}{\partial T} \right)_P dP.$$

For the computation, the present measurements were used from 5 kg/cm² to P_m , and those of Sherman and Edeskuty (29), from P_{sat} to 5 kg/cm². The results over 1.2° to 2.0°K showed the entropy of solid at the melting curve (or S_α) to rise only from 1.34 to 1.43 cal/deg/mol. Subtraction of the entropy change of compression and of transition in solid gave approximate S_β values of 1.32 to 1.34. The entropy associated with a nuclear spin system in completely random orientation is $S = R \ln 2 = 1.38$. It would appear that for solid He³ this is the major source of entropy.

The values of ΔS_m listed in Tables I and II were derived from the Clapeyron equation using experimental ΔV_m data and slopes computed from analytical expressions for the melting curves. For both He isotopes ΔS_m increases with P_m over the experimental range covered, although the increase becomes progressively smaller at higher melting pressures. This behavior is contrary to that of N₂ (15), which showed a decrease of ΔS_m with increasing P_m . Ebert (36), using melting properties for almost all materials studied to 1947 by Bridgman, found that ΔS_m and ΔV_m always decrease with rising P_m and, indeed, extrapolate to zero at some finite high pressure, a criterion of a critical point. The behavior of He then appears to be anomalous, at least up to 3555 kg/cm². The continued rise with pressure of ΔS_m is incompatible with the possibility of a critical point between solid and fluid. Since the question of a critical point in melting curves has yet to be resolved, it is interesting to extrapolate the He melting data to higher pressures than were measured.

An expression for ΔS_m at high pressures can be derived in terms of P_m by combining Eqs. (1) and (3). When $d\Delta S_m/dP_m$ is set equal to zero, one finds the solutions $P_m = 4219$ kg/cm² and $P_m = 3628$ kg/cm² for He³ and He⁴, respectively.

These melting pressures are only slightly higher than the present experimental range and represent pressures at which maxima occur in ΔS_m . At higher pressures ΔS_m decreases with P_m and finally extrapolates to zero at $P_m = 79,500$ kg/cm² ($T_m = 235^\circ\text{K}$) for He³ and $P_m = 63,900$ kg/cm² ($T_m = 197^\circ\text{K}$) for He⁴. Therefore, a critical point in the melting curve is not precluded by the available data. There is some indication that the melting thermal properties of the heliums become "normal" at sufficiently high pressures.

ACKNOWLEDGMENT

We wish to thank R. H. Sherman for assistance in fitting experimental data to analytical equations.

RECEIVED: March 23, 1959

REFERENCES

1. R. L. MILLS AND E. R. GRILLY, *Phys. Rev.* **99**, 480 (1955).
2. D. W. OSBORNE, B. M. ABRAHAM, and B. WEINSTOCK, *Phys. Rev.* **82**, 263 (1951); **85**, 158 (1952).
3. J. S. DUGDALE AND F. E. SIMON, *Proc. Roy. Soc.* **A218**, 268 (1953).
4. F. A. HOLLAND, J. A. W. HUGGILL, and G. O. JONES, *Proc. Roy. Soc.* **A207**, 268 (1951).
5. C. A. SWENSON, *Phys. Rev.* **89**, 538 (1953).
6. C. A. SWENSON, *Phys. Rev.* **86**, 870 (1952).
7. C. A. SWENSON, *Phys. Rev.* **79**, 626 (1950).
8. W. H. KEESOM AND J. H. C. LISSMAN, *Leiden Comm.* **232b** (1934).
9. W. H. KEESOM AND A. P. KEESOM, *Leiden Comm.* **224e** (1933).
10. W. H. KEESOM, "Helium," p. 210. Elsevier, Amsterdam, 1942.
11. F. SIMON, M. RUHEMANN, and W. A. M. EDWARDS, *Z. physik. Chem.* **B6**, 62 (1929), **B6**, 331 (1930).
12. F. SIMON, *Z. physik. Chem.* **B2**, 340 (1929).
13. F. E. SIMON AND C. A. SWENSON, *Nature* **165**, 829 (1950).
14. R. L. MILLS AND E. R. GRILLY, Proceedings of the Symposium on Liquid and Solid He³, The Ohio State University, August 20-23, 1957, p. 100; Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, University of Wisconsin, August 26-31, 1957, p. 106. Univ. of Wisconsin Press, Madison, 1958.
15. E. R. GRILLY AND R. L. MILLS, *Phys. Rev.* **105**, 1140 (1957).
16. O. C. BRIDGEMAN, *J. Am. Chem. Soc.* **49**, 1174 (1927).
17. C. H. MYERS AND R. H. JESSUP, *J. Research Natl. Bur. Standards* **6**, 1061 (1931).
18. R. L. MILLS, *Rev. Sci. Instr.* **27**, 332 (1956).
19. S. G. SYDORIAK AND T. R. ROBERTS, Proceedings of the Fifth International Conference on Low Temperature Physics and Chemistry, University of Wisconsin, August 26-31, 1957, p. 212. Univ. of Wisconsin Press, Madison, 1958.
20. R. L. MILLS AND E. R. GRILLY, *Phys. Rev.* **101**, 1246 (1956).
21. H. VAN DIJK AND M. DURIEUX, *Physica* **24**, 920 (1958); *Leiden Comm. Suppl.* **115a**.
22. R. WIEBE, V. L. GADDY, AND C. HEINS, *J. Am. Chem. Soc.* **53**, 1721 (1931).
23. P. W. BRIDGMAN, *Proc. Am. Acad. Arts Sci.* **E9**, 173 (1924).
24. A. F. SCHUCH, E. R. GRILLY, AND R. L. MILLS, *Phys. Rev.* **110**, 775 (1958).
25. L. GOLDSTEIN, *Phys. Rev.* **112**, 1483 (1958).