

and for nitrogen

$$P_m = 0.8427(T + 3.88)^{1.80905} - 1697 \text{ (bar)}, \quad (2c)$$

$$V_{f1} = 132.1/(T + 24.69)^{0.3154} \text{ (cm}^3\text{/mole)}, \quad (3c)$$

$$\Delta V = 85.4/(T - 26.55)^{0.981} \text{ (cm}^3\text{/mole)}. \quad (4c)$$

These equations fit the experimental data of Tables I and II to within the estimated accuracies of the data except for the nitrogen-melting pressures at 87.03 and 102.15 °K, where the calculated pressures are, respectively, 8 bar higher and 12 bar lower than the experimental values, and the methane fluid molar volume at 111.25 °K where the calculated value is 0.18 cm³/mole higher than the experimental value. Due to the high degree of correlation between the parameters in these equations, a number of different sets of parameters might represent the data nearly as well as those given in Eqs. (2)–(4), so no special significance should be attached to the exact values given here. [However, in using Eqs. (2)–(4) to represent the data, care should be taken to include all the significant figures given for the constants, or errors much greater than the quoted uncertainties may result.]

Equations (2b), (2c), (4b) and (4c) have been combined with the Clausius-Clapeyron equation (1) to derive entropy changes ΔS on melting, and from these the enthalpy changes $\Delta H = T\Delta S$ and internal energy changes $\Delta U = T\Delta S - P\Delta V$ on melting have also been calculated. These derived changes in thermodynamic variables are also listed in Tables I and II at the experimental temperatures. Values of these or any other melting parameters at any temperature (within the experimental ranges) can be readily calculated using Eqs. (2)–(4). Experience with noble gases,^{2,22,23} indicates that these equations should be valid for limited extrapolations to higher temperatures as well.

DISCUSSION

Stryland *et al.*²⁴ measured the P_m - T_m curve for methane up to 3 kbar and Clusius and Weigand²⁵ reported results up to 0.05 kbar. The results of Stryland *et al.* deviate from the present data systematically, with a maximum discrepancy of about 40 bar at 3 kbar. On an enlarged P_m - T_m plot, one can readily observe that their data do not extrapolate to the very reliable low-pressure data of Clusius and Weigand whose work has a claimed accuracy of better than 0.05%. Our results do extrapolate well on such a plot. This fact, coupled with the excellent agreement of our argon data² with results of other workers, seems to indicate that the present values are likely to be more reliable. There are no other high-pressure melting-volume data for comparison with our methane data.

The status of the nitrogen P_m - T_m data is as follows: Simon *et al.*,⁷ using the blocked-capillary method, and Robinson,¹⁰ using the moving-pellet

method, give results in agreement with each other. Bridgman,⁸ using the volume-discontinuity criterion, and Mills and Grilly,¹¹ using the blocked-capillary technique, report results in substantial agreement with the present work, but with pressures 8% lower than the previous two. In view of the deviations of Robinson's argon data from the highly accurate results of Hardy *et al.*²² and the general reliability of the melting work of Mills and Grilly, it is reasonable to assume that the present P_m - T_m values, along with those of Bridgman and Mills and Grilly represent the best available P_m - T_m data.

In the range over which the high pressure data of Table II overlap with the data of Grilly and Mills,⁶ the two fluid molar-volume data sets agree to within their combined uncertainties. However, near the triple point the present data as represented by Eq. (3c) deviate from those of Grilly and Mills by as much as 0.6%, with the present values being lower. This is entirely due to the present choice of triple-point V_{f1} , and a different choice of V_{f1} might significantly change the agreement over this range (approximately 65–70 °K). Taking account of the fact that the two sets of data were obtained at quite different times, at different laboratories, and with different techniques, the agreement between their data and ours is quite gratifying.

Grilly and Mills method was essentially a combination of a free-piston gauge for monitoring the freezing process and subsequent expansion into a metering system for determining absolute volumes. This method is more reliable than the piston displacement technique used by Bridgman.⁵ Bridgman's results appear to have some gross errors; they deviate from the other results by as much as 10%. (Similar deviations from Bridgman's data were observed earlier for argon.²⁶) Some of his errors may be accounted for by the fact that his low-temperature fluid densities were obtained indirectly by using high-pressure P - V - T relations for gas at room temperature; and that he apparently used, as temperature calibration baths, liquids N₂ and O₂ of unspecified purity. The agreement between the present results and Benedict's extrapolated values is as good as can be expected; the largest discrepancy is about 0.25%, about the same as the accuracy he claimed.

The only direct measurements which can be compared with our derived values of V_s at the triple point are those of Manzhelii and Tolkachev²⁷ who measured the molar volume of solid methane along its vapor-pressure curve at 77.4 and at 85.9 °K. A short linear extrapolation from these two points yields a triple-point molar volume of 33.01 cm³/mole which is 0.14 cm³/mole higher than the value given in Table I. This difference is again within the uncertainty involved in their original data and in the extrapolation to the triple point.

In conclusion, the present results make available for the first time rather complete and accurate high-pressure melting data for methane, and extend the range of similar existing data for nitrogen.

It is hoped that these data along with the earlier melting data for argon may be helpful in clarifying the effects which molecular rotational degrees of freedom have on melting in such simple systems.

*Work supported in part by the National Science Foundation under Grant Nos. GP-7739 and GP-18573 and in part by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-1198.

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¹R. K. Crawford and W. B. Daniels, *J. Chem. Phys.* **50**, 3171 (1969).

²V. M. Cheng, W. B. Daniels, and R. K. Crawford, *Phys. Lett. A* **43**, 109 (1973).

³M. S. Costantino, W. B. Daniels, and R. K. Crawford, *Phys. Rev. Lett.* **29**, 1098 (1972).

⁴W. F. Lewis, D. Benson, R. K. Crawford, and W. B. Daniels, *J. Phys. Chem. Solids* **35**, 383 (1974); W. F. Lewis, R. K. Crawford and W. B. Daniels, *ibid.* **35**, 1201 (1974).

⁵P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **70**, 1 (1935).

⁶E. R. Grilly and R. L. Mills, *Phys. Rev.* **105**, 1140 (1957).

⁷F. E. Simon, M. Ruhemann, and W. A. M. Edwards, *Z. Phys. Chem. B* **6**, 331 (1930).

⁸P. W. Bridgman, *Phys. Rev.* **46**, 930 (1934).

⁹M. J. Benedict, *J. Am. Chem. Soc.* **59**, 2233 (1937).

¹⁰D. W. Robinson, *Proc. R. Soc. A* **225**, 393 (1954).

¹¹R. L. Mills and E. R. Grilly, *Phys. Rev.* **99**, 480 (1955).

¹²V. M. Cheng, thesis (Princeton University, 1972) (unpublished).

¹³V. M. Cheng, R. K. Crawford, and W. B. Daniels, *Rev. Sci. Instrum.* **44**, 1401 (1973).

¹⁴*Thermodynamic Functions of Gases, Volume 3*, edited by F. Din (Butterworth, London 1961).

¹⁵D. R. Lovejoy, *Nature* **197**, 353 (1963).

¹⁶C. R. Barber, *Metrologia* **5**, 35 (1969).

¹⁷R. D. Goodwin and R. Prydz, *J. Res. Natl. Bur. Stds. A* **76**, 81 (1972).

¹⁸V. Mathot, L. A. K. Staveley, J. A. Young, and N. G. Parsonage, *Trans. Faraday Soc.* **52**, 1488 (1956).

¹⁹E. Mathias, C. A. Crommelin, and H. K. Onnes, *Leiden Comm. No. 145c*, (1914).

²⁰K. Clusius, *Z. Phys. Chem. B* **3**, 41 (1929).

²¹W. F. Giaque and J. O. Clayton, *J. Am. Chem. Soc.* **55**, 4875 (1933).

²²W. H. Hardy, R. K. Crawford, and W. B. Daniels, *J. Chem. Phys.* **54**, 1005 (1971).

²³R. K. Crawford and W. B. Daniels, *J. Chem. Phys.* **55**, 5651 (1971).

²⁴J. C. Stryland, J. E. Crawford, and M. A. Mastoor, *Can. J. Phys.* **38**, 1546 (1960).

²⁵K. Clusius and K. Weigand, *Z. Phys. Chem.* **46**, 1 (1940).

²⁶R. K. Crawford and W. B. Daniels, *Phys. Rev. Lett.* **21**, 367 (1968).

²⁷V. G. Manzhelii and A. M. Tolkachev, *Fiz. Tverd. Tela* **5**, 3413 (1963) [*Sov. Phys.-Sol. State* **5**, 2506 (1964)].