CHEN-VM 75-0141

PHYSICAL REVIEW B VOLUME 11, NUMBER 10 15 MAY 1975

Melting parameters of methane and nitrogen from 0 to 10 kbar*

V. M. Cheng[†]
Physics Department, Lafayette College, Easton, Pennsylvania 18042

W. B. Daniels
Physics Department, University of Delaware, Newark, Delaware 19711

R. K. Crawford
Physics Department and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

(Received 2 December 1974)

Fluid and solid molar volume and pressure-temperature melting data have been obtained at pressures up to 10 kbar for nitrogen and methane. These results have been combined with data from the literature to derive molar volumes of the solids at their respective triple points, and the resulting complete data sets have been represented by fitted empirical equations.

INTRODUCTION

In an earlier paper[1] a weighing apparatus and technique for precise determination of the P-V-T relations of gases at high pressures were described and data for argon were reported. The same apparatus has been rebuilt to render better temperature control, increased experimental stability, and extended pressure and temperature ranges. The improved arrangement has been used to measure the equation of state and melting parameters for argon, methane, and nitrogen up to 10.5 kbar and roughly between liquid-nitrogen and room temperatures. By melting parameters, we mean the P_m-T_m melting curve as well as the solid and fluid molar volumes along the melting curve. Data for argon[2] have been published elsewhere. Here we report the melting results for nitrogen and methane. Fluid equation-of-state data will be presented in a later publication.

There are at least two reasons for making these measurements. First, a set of accurate melting data for these simple substances might eventually play a significant role in the formulation of melting theories and lead to a deeper understanding of the melting process. Secondly, these results are essential complementary data in the interpretation of certain solid-phase experiments.[3,4] Prior to this work, very few high-pressure melting data were available for nitrogen and methane. There were virtually no volume-melting data for methane, and only two known molar-volume measurements[5,6] for N_2 along the melting curve. Bridgman's results[5] and those of Grilly and Mills[6] will be compared with the present work. Several workers[7–11] have measured the P_m-T_m melting curves for nitrogen and methane; these results will also be compared with ours.

Previously available values for the molar volumes of solid methane and nitrogen at their respective triple points are quite uncertain, so our results have been combined with data from the literature to calculate these molar volumes more accurately. The final complete sets of melting data (including triple-point data) have then been represented by least-squares-fit empirical equations to facilitate interpolation and to provide smooth values of derived thermodynamic functions along the melting curves.

EXPERIMENTAL

The basic weighing method has been described fully in the earlier paper.[1] Description of the present modifications to the original equipment can be found elsewhere[12,13] and will not be further discussed here. Altogether, melting data at seven different temperatures for methane and eight different temperatures for nitrogen have been obtained. The methane results range from 0.8 to 10.5 kbar, corresponding to approximate temperatures of 111 to 260 °K; the nitrogen data range from 1.2 to 10.2 kbar, corresponding to temperatures of 87 to 193 °K. Due to the particular nature of this experimental arrangement, the accuracy of the molar-volume measurements (the least well known of the three measured quantities—temperature, pressure, and volume) is higher for substances with higher molecular weights. Because of this, the *estimated* accuracies of the present measurements are as follows: at a given temperature molar volumes can be determined to within ±0.2% for nitrogen and ±0.3% for methane, and melting pressures can be measured with an accuracy of about ±5 bar. Detailed discussion of the technique and accuracy of temperature and pressure measurements is contained in Refs. 12 and 13.

Nitrogen gas of prepurified grade (99.998% pure)

TABLE I. Methane: thermodynamic functions at the melting curve. (Temperatures are in °K; pressures in bar; volumes in cm^3/mole; entropies in J/mole °K; enthalpies and energies in J/mole.)

T_m	P_m	V_{fl}	V_{sol}	ΔV	ΔS^a	ΔH^a	ΔU^a
90.688^b	0^b	35.53^b	32.87^b	2.66^b	10.3	935	935
111.25	867	33.63	31.75	1.88	8.8	975	807
131.80	1858	32.47	30.92	1.55	7.9	1040	753
156.97	3228	31.25	29.97	1.28	7.2	1130	728
180.36	4649	30.20	29.09	1.11	6.8	1219	724
212.02	6773	29.08	28.16	0.92	6.3	1341	736
237.58	8655	28.23	27.47	0.76	6.1	1440	752
260.85	10487	27.56	26.88	0.68	5.9	1529	771

$^a\Delta S$, ΔH, and ΔU were calculated at the temperatures given using Eqs. (2b) and (4b) of the text.

^{b}Sources for triple-point data are discussed in the text.

from Air Products and Chemicals, Inc. and methane gas of ultrahigh purity (99.97% pure) from Matheson Gas Products are used in this work.

The experimental melting data for methane and nitrogen are presented in Tables I and II along with triple-point data and some smoothed derived thermodynamic functions (see below).

TRIPLE-POINT DATA

It was considered desirable to include triple-point data in fitting the melting functions discussed below, so that the fitted functions could be used as reliable representations of the methane and nitrogen melting parameters from the triple points all the way up to 10 kbar. Consequently, a literature search was undertaken to find the "best" triple-point data currently available for methane and nitrogen. The triple-point pressures of both substances are of the order of 0.1 bar (Ref. 14) and so are negligible for the present work. The triple-point temperature of methane was measured accurately by Lovejoy[15] and when converted to the IPTS-68 temperature scale[16] it is (90.688 ± 0.005)°K. The triple-point temperature of nitrogen is given as a secondary fixed point on the IPTS-68 scale as 63.148 °K. The recent measurements of Goodwin and Prydz[17] appear to yield the most accurate value of the triple-point molar volume of liquid methane. Their value of 35.53 ± 0.03 cm^3/mole is in exact agreement with the earlier determination of Mathot *et al.*[18] The triple-point molar-volume values available for liquid nitrogen all involve somewhat uncertain extrapolations from the data. The value given by Din[14] based on an extrapolation of the data of Mathias *et al.*[19] is 32.22 cm^3/mole, and falls near the middle of the other available numbers. This value appears to be as good as any, but fairly large limits of uncertainty should be assumed.

Only a few molar-volume data are available for solid methane and nitrogen at high temperatures and these appear to be rather unreliable. Consequently, the changes in molar volume on melting at the triple point were calculated for methane and nitrogen from the Clausius-Clapeyron equation

$$\Delta V = \Delta S\left(\frac{dP_m}{dT_m}\right)^{-1}, \tag{1}$$

where ΔV and ΔS are, respectively, the volume and entropy changes on melting and dP_m/dT_m is the slope of the P_m-T_m melting curve (all evaluated at the melting temperature of interest). Values of dP_m/dT_m were obtained by differentiating the $P_m(T_m)$ melting equations (2b) and (2c) fit to the data of Tables I and II. Values of ΔS were obtained from the calorimetric latent heat measurements of Clusius[20] for methane ($\Delta S = 10.34$ J/mole °K) and of Giauque and Clayton[21] for nitrogen ($\Delta S = 11.42$ J/mole °K). The estimated uncertainty for the resulting ΔV values is about 0.05 cm^3/mole in both cases. These derived values for ΔV and the corresponding solid molar volumes V_s at the triple points are included in Tables I and II.

EMPIRICAL FUNCTIONS AND DERIVED MELTING DATA

Previously it was found that all the melting data for argon could be represented by the simple empirical functions[2,22]

$$P_m = 4.9931(T_m - 30.179)^{1.430\,57} - 1484.9 \text{ (bar)}, \tag{2a}$$

$$V_{fl} = 77.54/T_m^{0.229} \text{ (cm}^3\text{/mole)}, \tag{3a}$$

$$\Delta V = 19.41/(T_m - 59.40)^{0.527} \text{ (cm}^3\text{/mole)}. \tag{4a}$$

Similar functions have been least-squares fit to the methane and nitrogen melting data of Tables I and II (with the points weighted according to their estimated uncertainties). The resulting equations are for methane:

$$P_m = 1.7810(T - 18.16)^{1.608\,83} - 1753 \text{ (bar)}, \tag{2b}$$

$$V_{fl} = 103.9/(T + 0.65)^{0.2380} \text{ (cm}^3\text{/mole)}, \tag{3b}$$

$$\Delta V = 59.9/(T - 46.53)^{0.823} \text{ (cm}^3\text{/mole)}, \tag{4b}$$

TABLE II. Nitrogen: thermodynamic functions at the melting curve. (Units as in Table I.)

T_m	P_m	V_{fl}	V_{sol}	ΔV	ΔS^a	ΔH^a	ΔU^a
63.148^b	0^b	32.22^b	29.72^b	2.50^b	11.4	723	723
87.03	1239	29.80	28.26	1.54	9.0	779	588
102.15	2203	28.67	27.46	1.21	8.1	832	563
115.66	3130	27.81	26.77	1.04	7.6	883	556
131.14	4320	26.89	25.99	0.90	7.2	944	558
145.08	5496	26.19	25.39	0.80	6.7	1001	567
160.70	6915	25.44	24.74	0.70	6.6	1064	580
175.82	8404	24.78	24.16	0.62	6.4	1126	597
192.83	10195	24.20	23.63	0.57	6.2	1195	617

$^a\Delta S$, ΔH, and ΔU were calculated at the temperatures given using Eqs. (2c) and (4c) of the text.

^{b}Sources for triple-point data are discussed in the text.

and for nitrogen

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

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

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

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 cm^3/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 Weigand[25] 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 data[2] 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-discontinutiy 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 N_2 and O_2 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 Tolkachev[27] 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 cm^3/mole which is 0.14 cm^3/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.

†Present address: Space Div., General Electric Co., Box 8555, Philadelphia, Pa. 19101.

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

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

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

[4] W. 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).

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

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

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

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

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

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

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

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

[13] V. 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).

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

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

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

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

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

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

[21] W. F. Giauque and J. O. Clayton, J. Am. Chem. Soc. 55, 4875 (1933).

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

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

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

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

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

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