PHYSICAL REVIEW B VOLUME 11, NUMBER 10 15 MAY 1975

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

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(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]ΔS, 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

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

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]

$$P_m = 4.9931(T_m - 30.179)^{1.43057} - 1484.9 \text{ (bar)}, \qquad (2a)$$

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

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

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:

$$P_m = 1.7810(T - 18.16)^{1.60883} - 1753 \text{ (bar)}, \qquad (2b)$$

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

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

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]ΔS, 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.