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Volume Change on Melting of N₂ up to 3500 kg/cm²*

E. R. GRILLY AND R. L. MILLS

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico

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New and more accurate measurements were made of the volume change on melting of N₂ up to 3500 kg/cm². Liquid density and thermal expansion were also studied along the melting curve. A low-pressure metering system was used throughout. The ΔV_m data were fitted to the empirical equation, $\Delta V_m = A - B \log_{10}(P+C)$, with success. Combination of this equation with our previously reported melting equation yields expressions for ΔS and ΔH of melting useful up to 3500 kg/cm².

I. INTRODUCTION

IN a preceding paper¹ we presented accurate measurements of the melting curve of N₂ up to 3500 kg/cm². These data are especially useful if they can be combined with consistent measurements of ΔV_m , the volume change on melting, over a similar pressure range to yield values of the thermodynamic properties governing the melting process.

To date the only known ΔV_m measurements of N₂ are those reported by Bridgman² for the pressure range 1000-6000 kg/cm². Some of his experimental points show considerable deviation from a smooth line drawn through them and hence are unsuitable for the derivation of thermodynamic values from the melting curve mentioned above.

Recent speculation³ concerning the existence of a critical point in melting curves has heightened interest in better determinations of ΔV_m over a wide pressure range.

We report here accurate measurements of the volume change on melting of N₂ up to 3500 kg/cm². It is hoped that the program will be extended to include similar studies of He³, He⁴, H₂, D₂, T₂, Ne, and O₂.

II. EXPERIMENTAL

A. Apparatus

The apparatus finally adopted⁴ is shown schematically in Fig. 1. The hydraulic system which included a controlled-clearance free-piston gauge and mercury U-tube was identical to that described previously¹ with the exception that the lower pressure limit of the piston gauge was extended to 79 kg/cm². The high pressure N₂ loading system was also similar to that previously described except that a small compression cylinder was added to reach the higher pressures. Valves were commercial items which had been modified to have a minimum dead volume. The manganin resistance pres-

⁴ The first method tried was one of piston displacement in which the movement of the piston in a free-piston gauge was observed. Solid N₂ in a high-pressure cell was placed in pressure equilibrium with an oil system through a mercury U-tube. A controlled-clearance free-piston gauge was connected to the oil system. Piston height as a function of time was recorded to give the background rate of fall of the piston. This rate could be kept extremely small by a suitably high jacket pressure. Temperature of the cell was then raised slightly above the melting point which induced melting in the cell. The piston rose until all solid N₂ in the cell had melted after which the piston resumed its background rate of fall. A plot of piston height vs time, with corrections for leakage, made it possible to calculate the piston displacement and hence the ΔV of melting for the specific cell volume. The calculation however required a knowledge of the density of N₂ at room temperature as well as at its melting point. In practice it was found that reproducibility of ΔV_m measurements obtained in this way approached only $\pm 1\%$, and the method was abandoned in favor of the low-pressure metering system.

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¹ R. L. Mills and E. R. Grilly, *Phys. Rev.* **99**, 480 (1955).

² P. W. Bridgman, *Phys. Rev.* **46**, 930 (1934); *Proc. Am. Acad. Arts Sci.* **70**, 1-32 (1935).

³ L. Ebert, *Österr. Chem.-Ztg.*, No. 1/2, 1, (1954).

sure gauge has been described elsewhere⁶; in this application its sensitivity was 0.1 kg/cm². The high-pressure cell, nominally 0.3 cm³ in volume, was made of *AISI* No. 304 stainless steel welded shut at the bottom and had an inlet capillary silver-soldered in the top. All components in the high-pressure system were joined by *AISI* No. 347 stainless steel capillary 0.75 mm o.d. \times 0.15 mm i.d. where minimum dead volume was desirable. The low-pressure volume-manometer has been described previously.⁶

B. General Procedure

The following experimental technique was used in measuring ΔV_m . With valve 4 closed and valves 1, 2, and 3 open, the system was charged to some fixed pressure with N₂; then valve 1 was closed and the gas pressure was balanced against the free-piston gauge. The cryostat bath was lowered just out of contact with the high pressure cell, and the bath temperature was adjusted to some value between 0.3° and 1.0° lower than the equilibrium freezing point at that pressure. An automatic screw then raised the Dewar at the rate of 2 mm per minute until the bath covered the cell. From observations made of the rate of fall of the piston gauge, freezing in the cell could be verified. The piston was kept floating by means of an oil injector so that constant pressure prevailed during the freezing process. In this way, the cell was completely filled with solid from bottom to top. The manganin gauge was read, and valve 2 was then closed. Thereupon, current through the bath heater was increased, and the bath was warmed to a temperature \sim 0.5° above the equilibrium melting point. Melting in the cell was accompanied by a pressure rise observable with the manganin gauge. Valve 4 was then

cracked, and excess gas was bled into the low pressure metering system during the melting process. When melting was complete and the manganin gauge was brought to its initial reading, valve 4 was closed and valve 2 was opened to check the manganin gauge against the free-piston gauge for drift. Finally, the amount of excess gas removed was determined from *P-V-T* measurements at low pressure. From three to six separate ΔV_m determinations were made at each pressure.

A determination of the liquid coefficient of thermal expansion α_l (needed as a correction term) was made in the following way. The cell immersed in coolant bath was adjusted to a temperature slightly greater than the melting point. When pressure equilibrium had been established with the free-piston gauge, the manganin gauge reading was observed and valve 2 was closed. Bath temperature was raised \sim 2°; and excess gas, indicated by increased pressure on the manganin gauge, was bled via valve 4 into the volumetric system.

Absolute liquid density along the melting curve was determined as follows. With liquid in the cell balanced against the free-piston gauge, the bath temperature was adjusted to just above the melting temperature. Valve 3 was closed; valve 4 was opened; and the entire contents, high-pressure cell plus dead volume, were expanded into the metering system.

C. Temperature Measurements and Control

The methods and apparatus used here were essentially the same as those used in the melting curve measurements.¹ The baths, liquid N₂ up to 83°K, liquid O₂ in the 83–97° range, and liquid CH₄ above 97°, were controlled by a pneumatic manostat and stirred by a heater at the bottom of the bath. The thermometer was a copper-constantan thermocouple soldered to the top of the cell and calibrated *in situ* against vapor pressures of N₂ and O₂ which contained negligible amounts of impurities [see Sec. F of this paper for N₂ and Sec. 2B(g) (3) of the previous paper¹ for O₂]. An auxiliary thermocouple at the bottom of the cell was useful in eliminating thermal gradients in the bath.

The measurements of ΔV_m , V_l , and α_l were made as direct functions of pressure; however, as a check, the approximate melting temperatures were also determined during the ΔV_m experiments. They agreed to $\pm 0.05^\circ$ with those calculated from the pressure by means of our P_m vs T_m formula.¹

D. Volume Calibrations

The low-pressure volume-manometer was built and calibrated by Keller⁶ for his *P-V-T* work on the helium; his stated uncertainty contributes negligible error to the present measurements.

The volume of the experimental cell was determined from the weight of mercury required to fill it completely. Several determinations were made under slightly dif-

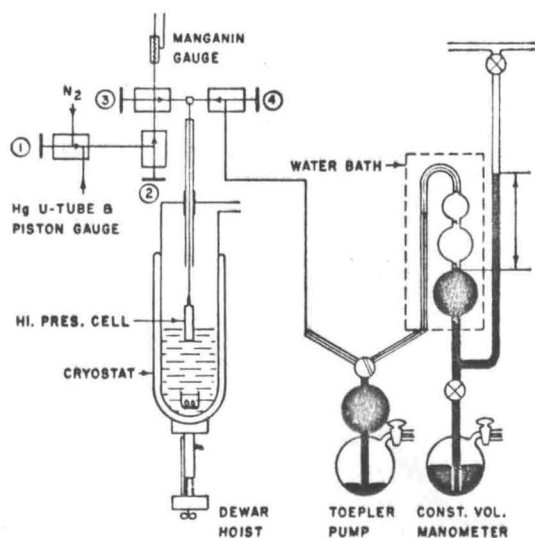


Fig. 1. A schematic diagram of the ΔV_m apparatus.

⁶ R. L. Mills and E. R. Grilly, *Phys. Rev.* **101**, 1246 (1956).

⁶ W. E. Keller, *Phys. Rev.* **97**, 1 (1955).

ferent conditions, but the results were consistent to 0.01%. After the cell had been leak tested at 3600 kg/cm², its volume increased 0.07%. To the final volume of 0.29405 cm³ at 1 atm and 300°K, corrections were made for: (1) the decrease caused by insertion of the capillary tube leading out of the bath (determined by geometry to be 0.00175 cm³); (2) the contraction with decrease in temperature; and (3) the expansion with increase in pressure. For (2), the linear thermal expansion coefficients of stainless steel AISI No. 304 measured by Altman, Rubin, and Johnston⁷ were used, giving a maximum correction of -0.9% at 60°K. To calculate (3), Eqs. (3.11) and (3.14) of Newitt⁸ for $\delta R/R$ and $\delta L/L$, respectively, were summed as $\delta V/V = \delta L/L + 2(\delta R/R)$. The computations were made with the 77°K value of Young's modulus, 27×10^6 psi, based on the work of Zambrow and Fontana⁹ on 18-8 steels and of the International Nickel Company¹⁰ on AISI No. 304 stainless steel. The value of Poisson's ratio was estimated¹¹ to be 0.30 ± 0.05 (where the possible error in the ratio is equivalent to $\pm 2.8\%$ of the correction). At 3500 kg/cm² the expansion correction amounted to +0.5% of the cell volume.

There were two dead volumes of concern to this research. The one of major importance, designated v_1 , was that volume included in the capillary "Tee" between the seats of valves 3 and 4, excluding the high-pressure cell. The quantity of gas contained in v_1 appears as a negative correction to the density determinations as discussed later in Sec. E. Dead volume v_2 was included between valves 2 and 4 with valve 3 open exactly one-half turn. This volume enters a small correction term for pressure mismatch, which is also discussed in Sec. E.

Volumes v_1 and v_2 were determined separately by filling them at room temperature with He to 1000 kg/cm² and then transferring the contents into the low-pressure volume-manometer. The determinations were carried out with a plug substituting for the high-pressure cell. Volumes were computed from densities for He reported by Wiebe, Gaddy, and Heins.¹² The results were $v_1 = 0.02222$ cm³ and $v_2 = 0.1860$ cm³.

E. Corrections

The quantity of gas in the dead volume v_1 during liquid density experiments was computed from P - V - T data for N₂ measured by Michels, Wouters, and de Boer¹³

and by Benedict.¹⁴ The calculation took account of the temperature gradient along the lead-in capillary, which was determined experimentally by thermocouples. The total dead volume correction varied with pressure from 0.8 to 6% of the liquid specific volume. The extrapolation from the experimental to the melting temperature was made with our thermal expansion coefficient and amounted to less than 0.1% of the specific volume.

The observation of the melting process actually involved the constant-pressure change in state as follows: solid at T_a → liquid at T_b . In order to get the volume change of melting, one must correct for the expansion due to warming of the solid from T_a to T_m and of the liquid from T_m to T_b . For the latter, the directly observed thermal expansion coefficient α_l was used; whereas for the expansion of the solid, an indirectly determined correction was obtained by freezing the nitrogen at different temperatures at the start of ΔV_m measurements, then choosing the α_s giving the most consistent values of ΔV_m . The expansion corrections amounted to 1 to 2% and 2 to 4% of ΔV_m for the liquid and solid, respectively.

In the event of pressure mismatch between the manganin gauge and free-piston gauge when valve 3 was opened after completion of a ΔV_m or α_l measurement, a knowledge of volume v_2 , in conjunction with density data,^{13,14} permitted calculation of the deficient or excess gas in the volume-manometer. This correction was as large as 1% of ΔV_m at 80 kg/cm², where N₂ compressibility is great, but it was essentially zero at 3500 kg/cm².

During the ΔV_m and α_l studies at 1920.7 kg/cm², a slight leak appeared in the system between valves 3 and 4, for which corrections were made from the observed

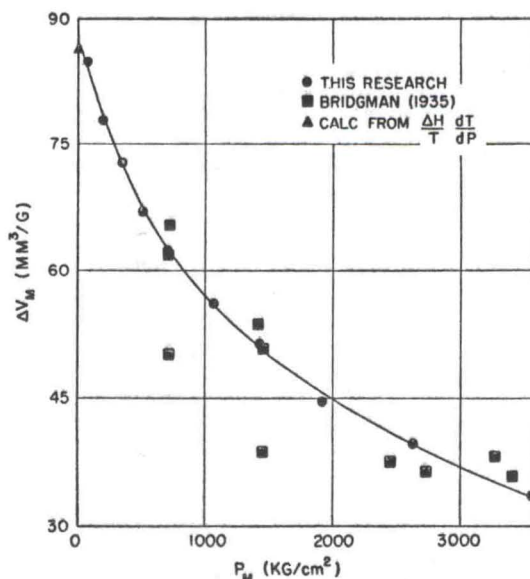


FIG. 2. The volume change on melting vs pressure for N₂.

⁷ Altman, Rubin, and Johnston of The Ohio State University; (private communication).

⁸ Dudley M. Newitt, *The Design of High Pressure Plant and the Properties of Fluids at High Pressures* (Oxford University Press, London, 1940), pp. 43-45.

⁹ J. L. Zambrow and M. G. Fontana, *Trans. Am. Soc. Metals* **41**, 480 (1949).

¹⁰ Reported by V. N. Krivobok in National Bureau of Standards Circular 520, 1952 (unpublished), p. 123.

¹¹ *Metals Handbook*, edited by Taylor Lyman (The American Society for Metals, Cleveland, Ohio, 1948), p. 431.

¹² Wiebe, Gaddy, and Heins, *J. Am. Chem. Soc.* **53**, 1721 (1931).

¹³ Michels, Wouters, and de Boer, *Physica* **3**, 585 (1936).

¹⁴ Manson Benedict, *J. Am. Chem. Soc.* **59**, 2224 (paper I); 2233 (paper II) (1937).

pressure drop, corresponding to a leak rate of 0.0108 cc (STP)/min. The leak corrections amounted to 11% of α_l and <1% of ΔV_m . The leak was located and repaired following the determinations at 1920.7 kg/cm², but another leak was observed during the measurements at 3555.6 kg/cm². Leak corrections here amounted to 52% of α_l and <3% of ΔV_m . It is estimated that the leak corrections at both pressures were known to $\pm 5\%$.

F. Purity of Nitrogen

The nitrogen was of Linde Air Products Company "spectroscopically pure" quality. Our mass spectrometer analysis showed that it contained 0.014% A, 0.005% O₂, <0.01% Ne, and <0.1% H₂. The rather poor limit set on the H₂ content results from the apparent contamination of the spectrometer; the real H₂ content was probably much less than 0.1%, for the melting point remained constant during the ΔV_m measurements even after several withdrawals of gas.

III. RESULTS

The general character of the data for the volume change on melting ΔV_m , the specific volume of the liquid V_l , and the thermal expansion coefficient of the liquid $\alpha_l \equiv (1/V_l)(\partial V_l/\partial T)_P$, on the melting curve, is shown by the curves of Figs. 2, 3, and 4. The experimental values of these properties and the derived thermal expansion coefficients of the solid α_s are given in Table I, which also includes the number of ΔV_m determinations made at each pressure and the degree of reproducibility. The accuracy of the measurements is

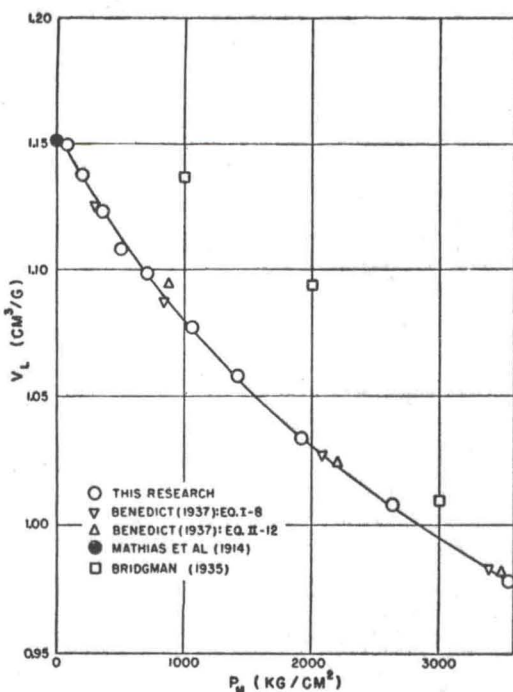


FIG. 3. The specific volume of liquid N₂ vs pressure along the melting curve.

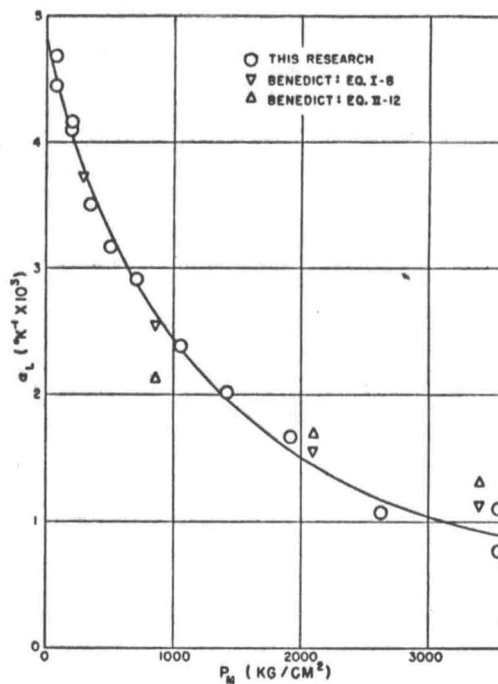


FIG. 4. The thermal expansion coefficient of liquid N₂ vs pressure along the melting curve.

estimated to be 0.5% for ΔV_m , 0.2% for V_l , and 2% for α_l .

Tammann¹⁵ has successfully expressed ΔV_m data by an empirical equation of the form

$$\Delta V_m = A - B \log_{10}(P+C). \quad (1)$$

The data of Table I were fitted to this equation by the method of least squares, and the three constants were evaluated as $A = 0.20707$ cm³/g, $B = 0.048457$ cm³/g, and $C = 275.98$ kg/cm² with a rms deviation in ΔV_m of 0.00043 cm³/g.

The specific volume and thermal expansion data could be represented by an equation of the type

$$x = b'(P+a')c', \quad (2)$$

where a' , b' , and c' are constants for the particular variable x . For the specific volume of the solid V_s , this form of equation has the attraction of possibly having theoretical significance, for its derivation from the Grüneisen equation of state and the Lindemann melting formula is similar to the derivation of the Simon melting equation,¹⁶

$$P = a + bT^c. \quad (3)$$

The constants of Eq. (2) for the various properties are given in Table II.

¹⁵ G. Tammann and G. Moritz, *Z. anorg. u. allgem. chem.* 218, 60 (1934).

¹⁶ L. Salter, *Phil. Mag.* 45, 369 (1954).

TABLE I. Properties of nitrogen along the melting curve.

P_m (kg/cm ²)	T_m (°K)	ΔV_m (mm ³ /g)	n^a	av dev. ^b (±%)	V_l (cm ³ /g)	α_l (10 ³ deg ⁻¹)	α_s (10 ³ deg ⁻¹)
1	63.14	(90.13) ^c					
79.0	64.84	84.65	4	0.42	1.1495	4.56	4.40
202.0	67.40	77.71	3	0.55	1.1376	4.14	4.03
354.7	70.46	72.69	4	0.37	1.1229	3.49	3.41
504.1	73.36	66.90	3	0.16	1.1081	3.17	3.12
710.9	77.24	62.34	6	0.58	1.0984	2.92	2.88
1066.8	83.57	55.91	4	0.16	1.0771	2.39	2.37
1422.7	89.54	51.24	6	0.27	1.0582	2.03	2.02
1920.7	97.40	44.50	4	0.26	1.0334	1.68	1.68
2631.9	107.83	39.71	4	0.31	1.0081	1.07	1.08
3555.6 (18503) ^c	120.29 (256.4) ^c	33.52 0	5	0.93	0.9782	0.94	0.95

^a n = number of ΔV_m determinations at each P_m .

^b The average deviation from the mean of the $n\Delta V_m$ determinations.

^c Values in parentheses are extrapolations of the measurements.

IV. DISCUSSION

A. Comparison with Previous Results

The only previous measurements of ΔV_m for N_2 were made by Bridgman² over the pressure range 1000–6000 kg/cm². His piston displacement method is considered less reliable than the present method in that his low-temperature fluid density was obtained indirectly by using high-pressure P - V - T relations for gas at room temperature. Furthermore, his temperature scale is in doubt, for he apparently used, as calibrating baths, liquid N_2 and O_2 of unspecified purity. Probably the most troublesome part of any method is in filling the cell completely with solid. Bridgman recognized this and sought to fill his cell completely by raising and lowering the bath around the cell. Even so, he concluded that his higher ΔV_m values were more reliable. In the present observations, it was found that the most reproducible data resulted from raising the freezing bath at a slow, uniform rate. A comparison of the present results with Bridgman's in Fig. 2 indicated fair agreement in general, although he reports several values that appear to be 25% too small. Also on the graph is the value of ΔV_m at 1 atmos calculated from the initial slope of the melting curve¹ and the ΔH_m of Giauque and Clayton¹⁷; it agrees to 0.7% with an extrapolation of the present measurements.

Figure 3 shows the present V_l data compared with: those extrapolated from Benedict's¹⁴ measurements (made at temperatures from 5 to 20° higher than T_m); the value at the triple point extrapolated from the measurements of Mathias *et al.*¹⁸ along the vapor pressure curve; and Bridgman's² measurements. The Benedict results¹⁴ covered a wide range of pressure and temperature and were put into two equations of state, Eq. (8) of Paper I and Eq. (2) of Paper II. Since the latter resulted from a more restricted range, it should not be expected to extrapolate as well to the melting

¹⁷ W. F. Giauque and J. O. Clayton, *J. Am. Chem. Soc.* **55**, 4875 (1933).

¹⁸ Mathias, Onnes, and Crommelin, *Leiden Comm. No. 145c* (1914).

curve. However, his Eq. (I-8) along with the Mathias value fit the present data within 0.2%, while Bridgman's values differ by as much as 6%.

The only comparative data on α_l result from differentiation of Benedict's equations of state and are given in Fig. 4. If one considers the extrapolation of his results and the accuracy of the present measurements, the agreement is adequate.

B. Formulas for Specific Volume and Thermal Expansion

A comparison of the constants of Eq. (2) with those of Eq. (3) indicates that the following relations should hold for V_s and possibly for V_l :

$$a' = a (= 1638),$$

$$b' = \frac{RT_0}{2a^{1/c}} \left(\frac{1+2c}{c-1} \right) (= 8.94),$$

$$c' = \frac{1}{c} - 1 (= -0.44),$$

where R is the gas constant, T_0 is the triple point temperature, and the numbers in parentheses are obtained from a , b , and c , the constants in the Simon melting equation for N_2 as measured previously.¹ It is readily apparent from Table II that there is some consistency in the relationships for a' of V_l , α_l , and α_s ; b' of V_l and V_s ; and c' of V_l and V_s . It is rather surprising that the a' for V_s , which should come closest to a , deviates the most.

C. Thermodynamic Properties of Melting

From the Clapeyron equation and Eqs. (1) and (3), one can obtain the following expressions for the thermal properties of melting,

$$\Delta H_m = c(P-a)[A - B \log_{10}(P+C)], \quad (4)$$

and

$$\Delta S_m = cb^{1/c}(P-a)^{(c-1)/c}[A - B \log_{10}(P+C)], \quad (5)$$

where, for N_2 ,

$$\begin{aligned} a &= -1638.3 \text{ kg/cm}^2, & A &= 0.20707 \text{ cm}^3/\text{g}, \\ b &= 0.97678 \text{ kg/cm}^2/\text{deg}, & B &= 0.048457 \text{ cm}^3/\text{g}, \\ c &= 1.7910, & C &= 257.98 \text{ kg/cm}^2. \end{aligned}$$

Up to 3500 kg/cm², the error in computed values of ΔH_m and ΔS_m should be <1%. At $P=1$ atmos, Eq. (4)

TABLE II. Constants in Eq. (2) for specific volumes and thermal expansion coefficients.

	a^* (kg/cm ²)	b^* (cm ³ /g or deg ⁻¹)	c^*
V_l	1695.3	3.4402	-0.14671
V_s	4486.5	5.8963	-0.20386
α_l	1904.0	754.1	-1.5851
α_s	2035.8	950.6	-1.6063

yields $\Delta H_m = 6.19$ cal/g, whereas the calorimetric value of Giaque and Clayton¹⁷ is 6.15 ± 0.05 cal/g; the agreement is satisfactory if one considers that Eq. (4) combines extrapolations of the melting curve below 23 kg/cm² and of ΔV_m below 79 kg/cm².

D. Question of a Critical Point in Melting Curves

In a review article, Bridgman¹⁹ summarized the experimental and theoretical work done on the fusion process, pointing out that the question remained as to whether the melting curve: (1) ends in a critical point; (2) rises to a maximum temperature and then falls; (3) rises to an asymptotic temperature; or (4) rises indefinitely with increasing pressure and temperature. Bridgman concluded, from his measurements²⁰ to 50 000 kg/cm² of melting phenomena and of the volumetric behavior of liquid and solid phases, that Hypothesis (4) is valid. Certain assumptions applied to the temperature-perturbed Thomas-Fermi atomic model led Gilvarry²¹ to predict a melting curve with normal behavior; i.e., with dP/dT always positive and always

increasing with P . In addition, he showed that $\Delta H_m/\Delta V_m$ always has a positive pressure coefficient, which is consistent with the absence of a critical point.

Recently Ebert,³ combining Bridgman's data with analogies drawn from the vaporization process, showed that, for certain substances, ΔS_m and ΔV_m might extrapolate to zero at the same pressure, a criterion of a critical point. It should be pointed out, however, that ΔS_m was calculated from P_m , T_m , and ΔV_m by means of the Clapeyron equation. Then if dP/dT remains finite, as required by the Simon melting equation, ΔV_m and ΔS_m must necessarily vanish at the same pressure. Since the Simon equation has been strengthened by several theoretical derivations,^{16,22-24} it is interesting to compute $P_m = 18\,500$ kg/cm² and $T_m = 256^\circ\text{K}$ from Eqs. (1) and (3) when $\Delta V_m = 0$ for N₂. These values indicate that the vanishing of ΔV_m might occur within the range of experimental pressures.

V. ACKNOWLEDGMENTS

We wish to thank W. E. Keller for the use of his volume-manometer and Max Goldstein for assistance in fitting the data to equations.

¹⁹ P. W. Bridgman, *Revs. Modern Phys.* **18**, 1 (1946).

²⁰ P. W. Bridgman, *J. Chem. Phys.* **9**, 794 (1941); *Proc. Am. Acad. Arts Sci.* **74**, 399 (1942).

²¹ J. J. Gilvarry, *Phys. Rev.* **102**, 317 (1956).

²² J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc. (London)* **A170**, 464 (1939).

²³ J. de Boer, *Proc. Roy. Soc. (London)* **A215**, 4 (1952).

²⁴ C. Domb, *Phil. Mag.* **42**, 1316 (1951).