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] ($\pm\%$)	V_l (cm^2/g)	α_l (10^3 deg^{-1})	α_s (10^3 deg^{-1})
1	63.14	(90.13)[e]					
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	120.29	33.52	5	0.93	0.9782	0.94	0.95
(18503)[e]	(256.4)[e]	0					

[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.
[e] 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 Bridgman[2] over the pressure range 1000–6000 kg/cm^2. 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 curve[1] and the ΔH_m of Giauque and Clayton[17]; 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's[14] 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's[2] measurements. The Benedict results[14] 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,

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

and

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

where, for N_2,

$a = -1638.3$ kg/cm^2, $A = 0.20707$ cm^3/g,
$b = 0.97678$ kg/cm^2/deg, $B = 0.048457$ cm^3/g,
$c = 1.7910$, $C = 257.98$ kg/cm^2.

Up to 3500 kg/cm^2, 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