

Figure 1 shows that if  $\sigma_1$  is very small compared with  $\sigma_2$ , then  $(X/R) - 1$  may be at least as great as about 0.2 even if the  $Q$  is nearly equal to the expected value. The assumption that  $X$  equals  $R$  could, therefore, lead to a systematic error in the application of Eq. (7) of as much as about 2 parts in  $10^6$  if  $Q$  were of the order of  $10^6$ . To reduce this error, an independent experiment must be performed to measure  $X/R$ .

#### IV. CONCLUSIONS

All of the measurements which are necessary to determine the velocity of light by a resonant cavity

can be made with sufficient accuracy to obtain a value correct to 1 part in  $10^6$  except the measurement of the surface reactance. Unless this quantity can be measured independently, or eliminated by the use of several modes at the same frequency, the velocity of light as measured by a resonant cavity cannot be justifiably stated with an uncertainty of less than 2 parts in  $10^6$ .

#### V. ACKNOWLEDGMENTS

The author expresses his appreciation to E. L. Ginzton and E. T. Jaynes for helpful discussions concerning this work.

### Volume Change on Melting of $N_2$ up to 3500 kg/cm<sup>2</sup>\*

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New and more accurate measurements were made of the volume change on melting of  $N_2$  up to 3500 kg/cm<sup>2</sup>. Liquid density and thermal expansion were also studied along the melting curve. A low-pressure metering system was used throughout. The  $\Delta V_m$  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  $\Delta S$  and  $\Delta H$  of melting useful up to 3500 kg/cm<sup>2</sup>.

#### I. INTRODUCTION

**I**N a preceding paper<sup>1</sup> we presented accurate measurements of the melting curve of  $N_2$  up to 3500 kg/cm<sup>2</sup>. These data are especially useful if they can be combined with consistent measurements of  $\Delta V_m$ , 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  $\Delta V_m$  measurements of  $N_2$  are those reported by Bridgman<sup>2</sup> for the pressure range 1000–6000 kg/cm<sup>2</sup>. 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 speculation<sup>3</sup> concerning the existence of a critical point in melting curves has heightened interest in better determinations of  $\Delta V_m$  over a wide pressure range.

We report here accurate measurements of the volume change on melting of  $N_2$  up to 3500 kg/cm<sup>2</sup>. It is hoped that the program will be extended to include similar studies of  $He^3$ ,  $He^4$ ,  $H_2$ ,  $D_2$ ,  $T_2$ ,  $Ne$ , and  $O_2$ .

\* Work done under the auspices of the U. S. Atomic Energy Commission.

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

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

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

#### II. EXPERIMENTAL

##### A. Apparatus

The apparatus finally adopted<sup>4</sup> 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 previously<sup>1</sup> with the exception that the lower pressure limit of the piston gauge was extended to 79 kg/cm<sup>2</sup>. The high pressure  $N_2$  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 manganese resistance pres-

<sup>4</sup> The first method tried was one of piston displacement in which the movement of the piston in a free-piston gauge was observed. Solid  $N_2$  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  $N_2$  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  $\Delta V$  of melting for the specific cell volume. The calculation however required a knowledge of the density of  $N_2$  at room temperature as well as at its melting point. In practice it was found that reproducibility of  $\Delta V_m$  measurements obtained in this way approached only  $\pm 1\%$ , and the method was abandoned in favor of the low-pressure metering system.

sure gauge has been described elsewhere<sup>5</sup>; in this application its sensitivity was 0.1 kg/cm<sup>2</sup>. The high-pressure cell, nominally 0.3 cm<sup>3</sup> 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.<sup>6</sup>

### B. General Procedure

The following experimental technique was used in measuring  $\Delta V_m$ . With valve 4 closed and valves 1, 2, and 3 open, the system was charged to some fixed pressure with N<sub>2</sub>; 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  $\Delta V_m$  determinations were made at each pressure.

A determination of the liquid coefficient of thermal expansion  $\alpha_l$  (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.<sup>1</sup> The baths, liquid N<sub>2</sub> up to 83°K, liquid O<sub>2</sub> in the 83–97° range, and liquid CH<sub>4</sub> 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 N<sub>2</sub> and O<sub>2</sub> which contained negligible amounts of impurities [see Sec. F of this paper for N<sub>2</sub> and Sec. 2B(g) (3) of the previous paper<sup>1</sup> for O<sub>2</sub>]. An auxiliary thermocouple at the bottom of the cell was useful in eliminating thermal gradients in the bath.

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

### D. Volume Calibrations

The low-pressure volume-manometer was built and calibrated by Keller<sup>6</sup> for his *P-V-T* work on the heliums; 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-

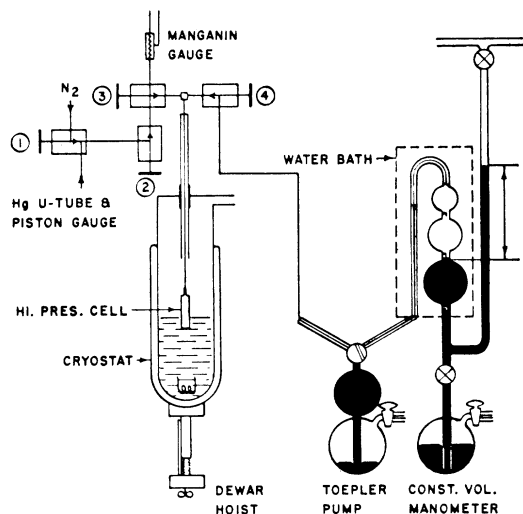


FIG. 1. A schematic diagram of the  $\Delta V_m$  apparatus.

<sup>5</sup> R. L. Mills and E. R. Grilly, *Phys. Rev.* **101**, 1246 (1956).

<sup>6</sup> 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/cm<sup>2</sup>, its volume increased 0.07%. To the final volume of 0.29405 cm<sup>3</sup> 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 cm<sup>3</sup>); (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 Johnston<sup>7</sup> were used, giving a maximum correction of -0.9% at 60°K. To calculate (3), Eqs. (3.11) and (3.14) of Newitt<sup>8</sup> 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,  $27 \times 10^6$  psi, based on the work of Zambrow and Fontana<sup>9</sup> on 18-8 steels and of the International Nickel Company<sup>10</sup> on AISI No. 304 stainless steel. The value of Poisson's ratio was estimated<sup>11</sup> to be  $0.30 \pm 0.05$  (where the possible error in the ratio is equivalent to  $\pm 2.8\%$  of the correction). At 3500 kg/cm<sup>2</sup> 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/cm<sup>2</sup> 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.<sup>12</sup> The results were  $v_1 = 0.02222$  cm<sup>3</sup> and  $v_2 = 0.1860$  cm<sup>3</sup>.

### E. Corrections

The quantity of gas in the dead volume  $v_1$  during liquid density experiments was computed from  $P$ - $V$ - $T$  data for N<sub>2</sub> measured by Michels, Wouters, and de Boer<sup>13</sup>

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

<sup>8</sup> 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.

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

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

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

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

<sup>13</sup> Michels, Wouters, and de Boer, *Physica* **3**, 585 (1936).

and by Benedict.<sup>14</sup> 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  $\alpha_l$  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  $\Delta V_m$  measurements, then choosing the  $\alpha_s$  giving the most consistent values of  $\Delta V_m$ . The expansion corrections amounted to 1 to 2% and 2 to 4% of  $\Delta V_m$  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  $\Delta V_m$  or  $\alpha_l$  measurement, a knowledge of volume  $v_2$ , in conjunction with density data,<sup>13,14</sup> permitted calculation of the deficient or excess gas in the volume-manometer. This correction was as large as 1% of  $\Delta V_m$  at 80 kg/cm<sup>2</sup>, where N<sub>2</sub> compressibility is great, but it was essentially zero at 3500 kg/cm<sup>2</sup>.

During the  $\Delta V_m$  and  $\alpha_l$  studies at 1920.7 kg/cm<sup>2</sup>, a slight leak appeared in the system between valves 3 and 4, for which corrections were made from the observed

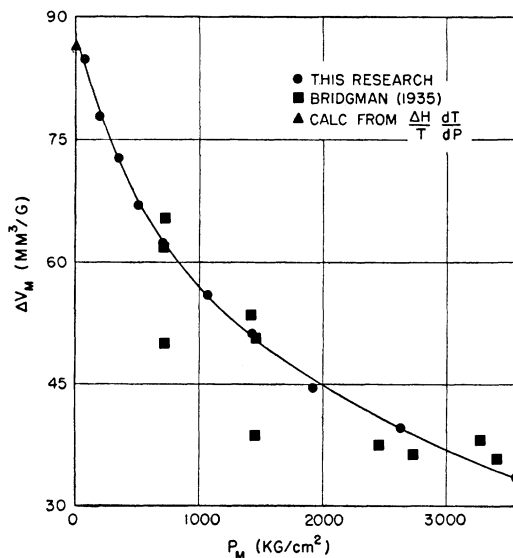


FIG. 2. The volume change on melting vs pressure for N<sub>2</sub>.

<sup>14</sup> 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  $\alpha_l$  and <1% of  $\Delta V_m$ . The leak was located and repaired following the determinations at 1920.7 kg/cm<sup>2</sup>, but another leak was observed during the measurements at 3555.6 kg/cm<sup>2</sup>. Leak corrections here amounted to 52% of  $\alpha_l$  and <3% of  $\Delta V_m$ . 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% O<sub>2</sub>, <0.01% Ne, and <0.1% H<sub>2</sub>. The rather poor limit set on the H<sub>2</sub> content results from the apparent contamination of the spectrometer; the real H<sub>2</sub> content was probably much less than 0.1%, for the melting point remained constant during the  $\Delta V_m$  measurements even after several withdrawals of gas.

### III. RESULTS

The general character of the data for the volume change on melting  $\Delta V_m$ , 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  $\alpha_s$  are given in Table I, which also includes the number of  $\Delta V_m$  determinations made at each pressure and the degree of reproducibility. The accuracy of the measurements is

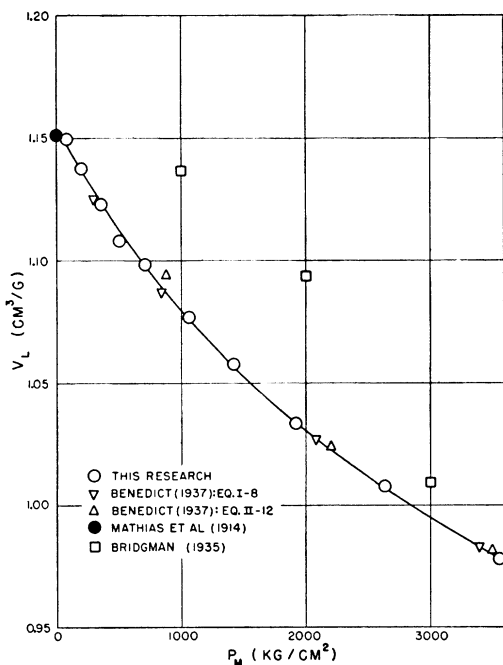


FIG. 3. The specific volume of liquid N<sub>2</sub> vs pressure along the melting curve.

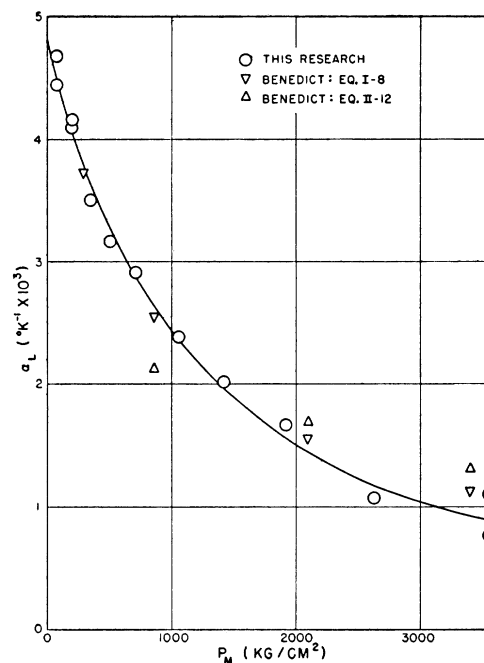


FIG. 4. The thermal expansion coefficient of liquid N<sub>2</sub> vs pressure along the melting curve.

estimated to be 0.5% for  $\Delta V_m$ , 0.2% for  $V_l$ , and 2% for  $\alpha_l$ .

Tammann<sup>15</sup> has successfully expressed  $\Delta V_m$  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  $A = 0.20707$  cm<sup>3</sup>/g,  $B = 0.048457$  cm<sup>3</sup>/g, and  $C = 275.98$  kg/cm<sup>2</sup> with a rms deviation in  $\Delta V_m$  of 0.00043 cm<sup>3</sup>/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,<sup>16</sup>

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

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

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

<sup>16</sup> L. Salter, Phil. Mag. **45**, 369 (1954).

TABLE I. Properties of nitrogen along the melting curve.

$P_m$ (kg/cm <sup>2</sup> )	$T_m$ (°K)	$\Delta V_m$ (mm <sup>3</sup> /g)	$n^a$	av dev. <sup>b</sup> (±%)	$V_l$ (cm <sup>3</sup> /g)	$\alpha_l$ (10 <sup>3</sup> deg <sup>-1</sup> )	$\alpha_s$ (10 <sup>3</sup> deg <sup>-1</sup> )
1	63.14	(90.13) <sup>c</sup>					
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) <sup>c</sup>	120.29 (256.4) <sup>c</sup>	33.52 0	5	0.93	0.9782	0.94	0.95

<sup>a</sup>  $n$  = number of  $\Delta V_m$  determinations at each  $P_m$ .

<sup>b</sup> The average deviation from the mean of the  $n\Delta V_m$  determinations.

<sup>c</sup> Values in parentheses are extrapolations of the measurements.

#### IV. DISCUSSION

##### A. Comparison with Previous Results

The only previous measurements of  $\Delta V_m$  for N<sub>2</sub> were made by Bridgman<sup>2</sup> over the pressure range 1000–6000 kg/cm<sup>2</sup>. 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<sub>2</sub> and O<sub>2</sub> 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  $\Delta V_m$  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  $\Delta V_m$  at 1 atmos calculated from the initial slope of the melting curve<sup>1</sup> and the  $\Delta H_m$  of Giaque and Clayton<sup>17</sup>; 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<sup>14</sup> 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.*<sup>18</sup> along the vapor pressure curve; and Bridgman's<sup>2</sup> measurements. The Benedict results<sup>14</sup> 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

<sup>17</sup> W. F. Giaque and J. O. Clayton, *J. Am. Chem. Soc.* **55**, 4875 (1933).

<sup>18</sup> 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  $\alpha_l$  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  $V_l$ :

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

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

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

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<sub>2</sub> as measured previously.<sup>1</sup> It is readily apparent from Table II that there is some consistency in the relationships for  $a'$  of  $V_l$ ,  $\alpha_l$ , and  $\alpha_s$ ;  $b'$  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<sub>2</sub>,

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

Up to 3500 kg/cm<sup>2</sup>, the error in computed values of  $\Delta H_m$  and  $\Delta S_m$  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 <sup>2</sup> )	$b'$ (cm <sup>3</sup> /g or deg <sup>-1</sup> )	$c'$
$V_l$	1695.3	3.4402	-0.14671
$V_s$	4486.5	5.8963	-0.20386
$\alpha_l$	1904.0	754.1	-1.5851
$\alpha_s$	2035.8	950.6	-1.6063

yields  $\Delta H_m = 6.19$  cal/g, whereas the calorimetric value of Giauque and Clayton<sup>17</sup> is  $6.15 \pm 0.05$  cal/g; the agreement is satisfactory if one considers that Eq. (4) combines extrapolations of the melting curve below 23 kg/cm<sup>2</sup> and of  $\Delta V_m$  below 79 kg/cm<sup>2</sup>.

#### D. Question of a Critical Point in Melting Curves

In a review article, Bridgman<sup>19</sup> 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 measurements<sup>20</sup> to 50 000 kg/cm<sup>2</sup> 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 Gilvarry<sup>21</sup> 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,<sup>3</sup> combining Bridgman's data with analogies drawn from the vaporization process, showed that, for certain substances,  $\Delta S_m$  and  $\Delta V_m$  might extrapolate to zero at the same pressure, a criterion of a critical point. It should be pointed out, however, that  $\Delta S_m$  was calculated from  $P_m$ ,  $T_m$ , and  $\Delta V_m$  by means of the Clapeyron equation. Then if  $dP/dT$  remains finite, as required by the Simon melting equation,  $\Delta V_m$  and  $\Delta S_m$  must necessarily vanish at the same pressure. Since the Simon equation has been strengthened by several theoretical derivations,<sup>16,22-24</sup> it is interesting to compute  $P_m = 18\,500$  kg/cm<sup>2</sup> and  $T_m = 256^\circ\text{K}$  from Eqs. (1) and (3) when  $\Delta V_m = 0$  for N<sub>2</sub>. These values indicate that the vanishing of  $\Delta V_m$  might occur within the range of experimental pressures.

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## Superposition (Double-Life) Model of Liquid Helium†

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London's idea of representing the liquid state by a superposition of phonon and translational modes of motion is generalized. The superposition procedure is given a rigorous quantum mechanical basis, and a statistical mechanical method is used to derive the superposition ratio for both isotopes of liquid helium; the ratio is correlated successfully with the thermodynamic data.

### INTRODUCTION

IN his second volume on superfluids,<sup>1</sup> London gave some very convincing reasons for doubting the essential significance of Landau's quantum hydrodynamics as an explanation of the anomalous behavior of liquid helium. Pragmatically the most compelling points are (a) that quantum hydrodynamics ought to be equally applicable to all liquids, and would predict substantially the same behavior for He<sup>3</sup> as for He<sup>4</sup>, and (b) that no explanation is offered by the theory for the

lambda transition above which the anomaly ceases to exist. *A priori*, quantum hydrodynamics is clearly no better than a quantum formalization of the classical continuum approximation to liquid theory: it substitutes a fictitious continuous field for the microscopic actuality, and there is little reason to believe that a quantized fiction is any better than the classical one.

As a tentative alternative procedure, London suggested (reference 1, p. 107) an additive superposition of translational modes of motion on the one hand and longitudinal vibrational modes (phonons) on the other. The phonons on London's picture represent the low-energy excitations and make appreciable contributions only at the lowest temperatures,  $T \ll T_\lambda$ ; while the translational modes, described in terms of Bose-Einstein gas theory, dominate near the lambda temperature. The

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<sup>1</sup> F. London, *Superfluids* (John Wiley and Sons, Inc., New York, 1954), Vol. II.