

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

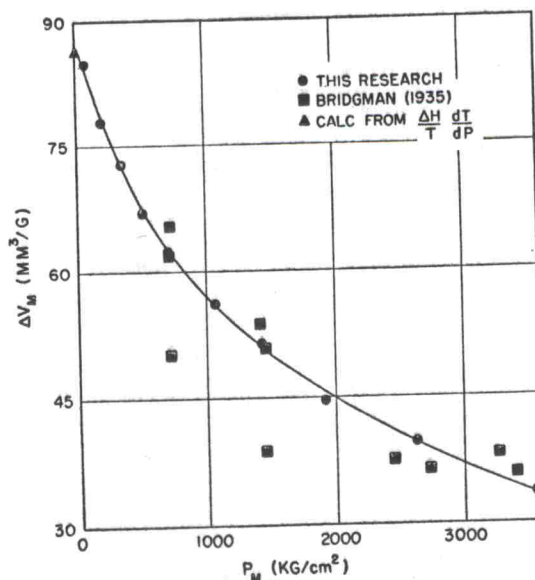


FIG. 2. The volume change on melting vs pressure for N<sub>2</sub>.

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