

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

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).

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

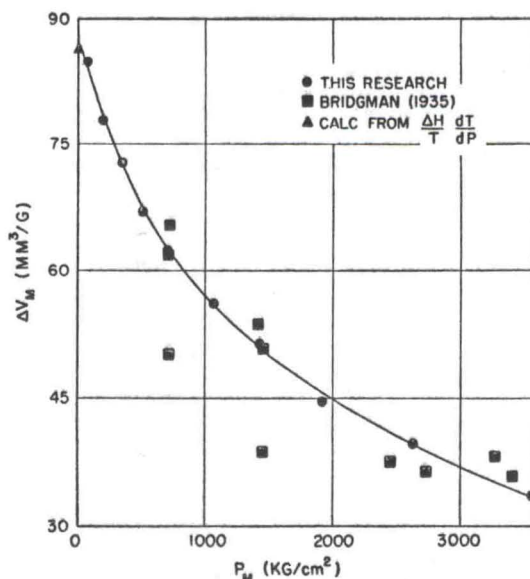


FIG. 2. The volume change on melting vs pressure for N₂.

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