

sure gauge has been described elsewhere<sup>6</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  $\sim 0.5^\circ$  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  $\sim 2^\circ$ ; 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 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-

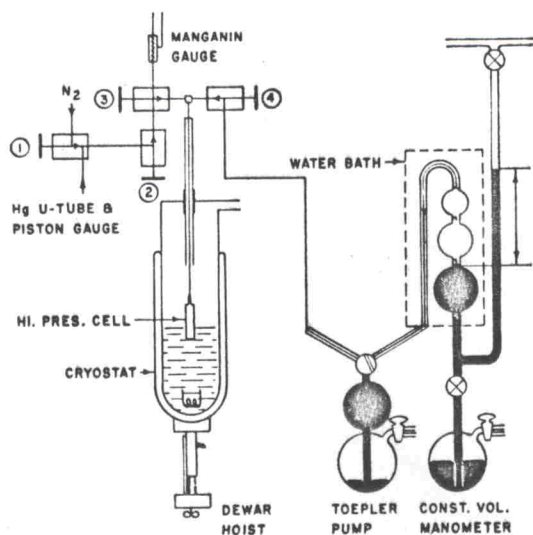


FIG. 1. A schematic diagram of the  $\Delta V_m$  apparatus.

<sup>6</sup> R. L. Mills and E. R. Grilly, Phys. Rev. 101, 1246 (1956).  
<sup>6</sup> W. E. Keller, Phys. Rev. 97, 1 (1955).