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# Volume Change on Melting of $N_2$ up to 3500 kg/cm²*

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New and more accurate measurements were made of the volume change on melting of $N_2$ up to 3500 kg/cm². 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/cm².

## I. INTRODUCTION

In a preceding paper[1] we presented accurate measurements of the melting curve of $N_2$ up to 3500 kg/cm². 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[2] for the pressure range 1000–6000 kg/cm². 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[3] 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/cm². 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 $O_2$.

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[1] R. L. Mills and E. R. Grilly, Phys. Rev. 99, 480 (1955).

[2] P. W. Bridgman, Phys. Rev. 46, 930 (1934); Proc. Am. Acad. Arts Sci. 70, 1–32 (1935).

[3] L. Ebert, Österr. Chem.-Ztg., No. 1/2, 1, (1954).

## II. EXPERIMENTAL

### A. Apparatus

The apparatus finally adopted[4] 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[1] with the exception that the lower pressure limit of the piston gauge was extended to 79 kg/cm². 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 manganin resistance pres-

[4] 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.