

yields $\Delta H_m = 6.19$ cal/g, whereas the calorimetric value of Giaque and Clayton¹⁷ is 6.15 ± 0.05 cal/g; the agreement is satisfactory if one considers that Eq. (4) combines extrapolations of the melting curve below 23 kg/cm^2 and of ΔV_m below 79 kg/cm^2 .

D. Question of a Critical Point in Melting Curves

In a review article, Bridgman¹⁹ 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 measurements²⁰ to $50\,000 \text{ kg/cm}^2$ 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 Gilvarry²¹ 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,³ combining Bridgman's data with analogies drawn from the vaporization process, showed that, for certain substances, ΔS_m and ΔV_m might extrapolate to zero at the same pressure, a criterion of a critical point. It should be pointed out, however, that ΔS_m was calculated from P_m , T_m , and ΔV_m by means of the Clapeyron equation. Then if dP/dT remains finite, as required by the Simon melting equation, ΔV_m and ΔS_m must necessarily vanish at the same pressure. Since the Simon equation has been strengthened by several theoretical derivations,^{16,22-24} it is interesting to compute $P_m = 18\,500 \text{ kg/cm}^2$ and $T_m = 256^\circ\text{K}$ from Eqs. (1) and (3) when $\Delta V_m = 0$ for N₂. These values indicate that the vanishing of ΔV_m might occur within the range of experimental pressures.

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