

These results agree with our present measurements on helium in so far as the entropy of the solid always rises along the melting curve with increasing temperature. There would, of course, be no objection from the thermodynamic point of view to this curve *falling* with rising temperature, and the result is therefore not trivial. It indicates that the effect of the rising temperature on the entropy surpasses the effect of the rise in Debye  $\theta$  associated with the increase of pressure; in other words, the temperature of the solid, measured in terms of the characteristic temperature, rises along the melting curve. Now with helium, the entropy obviously cannot fall below its value at absolute zero. It is also obvious that as the melting pressure remains practically constant up to about the  $\lambda$  point the entropy is bound to rise in this region. There is no reason, however, why the curve should not from then onwards approach the zero line again. The fact that it does not do so seems to be just as valid an indication that  $T/\theta$  (and therefore the entropy) rises along the melting curve as if it were happening in the 'classical' region—all the more so as the rise continues over such an enormous temperature range.

These experiments therefore lend additional strong support to a tentative statement proffered by one of us (Simon 1937) for normal substances (and according to Bridgman all substances tend towards normal behaviour at very high pressures), namely, that it is impossible to melt a substance by adiabatic, reversible compression, as such a compression would lead further into the range of stability of the solid. This statement may be of some interest in astrophysical and geophysical considerations.

*Note added in proof, 28 May 1953.* Since this paper was submitted, Mr L. Salter of the Clarendon Laboratory has succeeded in establishing equation (1) theoretically under more general conditions; no particular model of the melting process is needed, the substances are not assumed to be classical, and the range of validity is not restricted to high pressures. The basic assumptions are that the substance obeys the Grüneisen equation of state, that is,  $C_v = f(T/\theta)$ ,  $\theta = \phi(V)$ , and that the Lindemann melting formula is obeyed along the melting curve, a fact proved by the present experiments. The derivation relates the parameter  $c$  in equation (1) to Grüneisen's  $\gamma$ ,

$$\gamma \equiv -\frac{d \ln \theta}{d \ln V} = -\left(\frac{\partial \ln T}{\partial \ln V}\right)_S.$$

These results allow us to determine the condition for  $\frac{d}{dT} \left(\frac{T_m}{\theta}\right) > 0$  in terms of  $\gamma$ ; for substances which satisfy the two restrictions underlying Salter's derivation, the condition is simply  $\gamma > \frac{2}{3}$ . This value, it may be recalled, is the theoretical limiting value of  $\gamma$  as  $V \rightarrow \infty$ , i.e. for a gas; experimentally,  $\gamma$  values for regular crystals are found to lie between 1.5 and 2.5. These considerations, then, give theoretical support for the contention that melting cannot be achieved solely by reversible adiabatic compression.

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