

Strong and Bundy would seem to indicate that the equation has real physical validity. However, it would seem equally clear that the physical nature of the Simon constants is not as yet understood. Simon sought to relate the coefficient a to the "internal pressure" by the relationship $a = \Delta E/V$ where ΔE is taken to be approximately equal to the heat of vaporization or sublimation, and V is the atomic volume. Using the values $\Delta E = 57.5$ kcal/g-atom, $V = 15.7$ cm³/g-atom for indium, and $\Delta E = 70.0$ kcal/g-atom, $V = 16.3$ cm³/g-atom for tin,¹⁸ one obtains $a = 151\,000$ atm for indium and $a = 177\,000$ atm for tin, which are not even of the same order of magnitude as the experimental values. Also, the relationship $c = (6\gamma + 1)/(6\gamma - 2)$ between the Simon c and the Gruneisen γ , which was derived by both Salter⁵ and Gilvarry,⁶ gives values of c considerably too low for any of the metals. On the other hand, the value of c determined for tin comes very close to the smooth curve through the points representing the alkali metals and the Group VIII metals on the c - γ plot of Strong and Bundy.¹⁰ This corroborates their suggestion that some definite functional relationship exists between c and γ . The point representing indium, however, falls in the neighborhood of the rhodium point, far from either curve. Of course, the calculated value of the Gruneisen constant¹⁹ may well be in error because of its dependence upon the compressibility and the thermal expansion, both of which are evidently quite difficult to measure in the case of indium.

It would seem rather significant that the Simon equation can be applied equally as well to both phases of tin. In considering its application to the high-pressure phase, it becomes rather difficult to give the constant a any physical meaning, since the curve extrapolates to a

temperature of absolute zero on the pressure axis at a positive pressure of 16 200 atm. It would be interesting to see if the Simon equation fits the fusion curves of other high-pressure phases of polymorphic substances, such as those of bismuth. All in all, it begins to appear that the Simon relationship may be some sort of an inherent fundamental property of fusion curves, in addition to having validity as an interpolation formula.

One other question which arises in connection with the ultimate behavior of any fusion curve is that of the possible existence of a liquid-solid critical point, analogous to the gas-liquid critical point. Such a point would necessarily be characterized by the vanishing of both the latent heat of fusion and the volume change of the sample in melting. No indication either in favor of or against such a phenomenon was indicated by these experiments. With this particular experimental arrangement, it was impossible to make measurements of either changes in sample volume or latent heat of fusion. The relatively small volume change of the sample upon melting was evidently absorbed by the large volume of compressible pyrophyllite in the tetrahedral sample-holder, and the heat loss through the large anvils was great enough to effectively mask any latent heat effects. (For example, when the sample was melted, and the heating power suddenly cut off, the temperature dropped very fast to the ambient level, without a break in the cooling curve.) Therefore, the only indication of approaching a critical point that would be given by this experiment would be a lessening of the "avalanche effect" on the temperature as the sample is melted. (Even this would be inconclusive, since it could conceivably be affected by volume change and latent heat in such a way as to compensate for the effect of the resistance change.) However, such an indication was not given in this case, with either the indium or the tin. With both metals, the percentage increase in temperature upon melting was approximately constant over the entire pressure range.

¹⁸ J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes* (Reinhold Publishing Corporation, New York, 1950), 3rd edition, p. 323.

¹⁹ See E. Gruneisen, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1926), Vol. 10, pp. 1-59.