the pressure axis, with no observable tendency to approach either a maximum or a horizontal asymptote. No indication of polymorphism is observed. The data can be fitted very well by the Simon fusion equation:

$$P/15\,000\ \text{atm}=(T/429°\text{K})^{4.34}-1, \qquad (2)$$

the corrected melting temperatures never varying more than 1% from this curve. The values of the constants in Eq. (2) were determined by the method of least squares. In order to estimate the uncertainty in these values, the Simon equation was also fitted by the method of least squares to the maximum and minimum curves, which were drawn through the extremities of the range of uncertainty for the measured melting temperatures. The results indicated that a could vary as much as $\pm 20\%$, while c changed only by $\pm 2\%$.

By way of comparison, Butuzov and Ponyatovskii[16] found a nearly linear change up to a melting point of 280°C at 30 000 kg/cm², with a mean increase of 4.13×10^{-3} deg/kg/cm². The curve obtained here shows definite curvature in that range, exhibiting a melting temperature of 275°C at 30 000 kg/cm² (29 000 atm), with a mean increase of 3.96×10^{-3} deg/kg/cm². The values are in agreement to well within the experimental uncertainty.

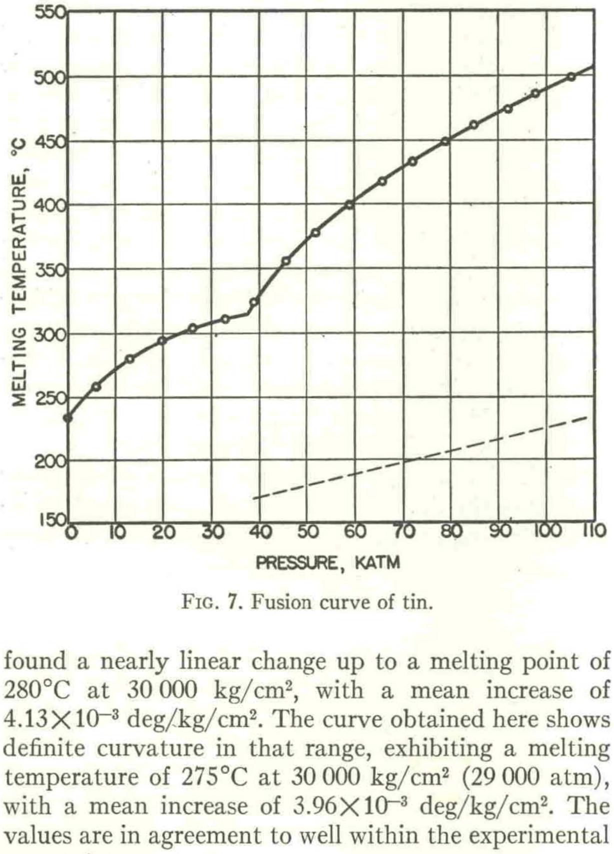

FIG. 7. Fusion curve of tin.

The experimental fusion curve for tin is shown in Fig. 7. A phase transition is indicated, with a triple point at about 38 000 atm and 318°C. The curve of the first phase rises smoothly from the normal melting temperature of 232°C at atmospheric pressure to the triple point, where a discontinuity in slope occurs. (This discontinuity was found to be reversible, and occurred consistently at the same pressure for all samples.) The fusion curve of the second phase rises smoothly from the triple point to a melting temperature of about 500°C at 105 000 atm. The curves of both phases seem to be normal in the sense of Bridgman (with the exception, of course, that the curve of the first phase does not continue indefinitely). The data for the first phase can be fitted well by the Simon equation:

$$P/7400\ \text{atm}=(T/505°\text{K})^{11.3}-1, \qquad (3)$$

and the data for the second phase by the equation:

$$(P-38\,000)/21\,800=(T/591)^{5.25}-1, \qquad (4)$$

where T_0 in the transformed Simon equation for the second phase is taken to be the triple-point temperature, or 591°K. The percentage uncertainties in the Simon coefficients and exponents are about the same as those for the corresponding values in the indium equation.

These results can be compared to those of Butuzov and Gonikberg,[17] who reported a melting temperature of 309°C at 30 000 kg/cm² (29 000 atm) for tin. The value indicated at that pressure by the data of this experiment is also 309°C. Butuzov and Gonikberg only carried their experiments to 34 000 kg/cm² (32 900 atm), and hence did not detect the phase change to a higher pressure modification.

An experimental attempt was also made to determine the phase structure of tin below the fusion curve, without complete success. The electrical resistance of the sample was determined as a function of temperature (at constant pressure) up to the melting point for each of the pressures at which the melting temperature was measured, and consistent discontinuities in these curves were sought. There was some indication (by a change in slope of the resistance vs temperature curve, which seemed to appear fairly consistently over a certain pressure range) that a phase transition-equilibrium line might exist as shown by the dashed line in Fig. 7. There is considerable uncertainty in the exact position and curvature of the line, which may of course be partly due to a possible tendency of the lower temperature phase to superheat into a region of instability and therefore not consistently indicate a phase transition at the point of equilibrium. No consistent indications of phase transitions were detected at pressures below those covered by the dashed line of Fig. 7, and the phase structure in the neighborhood of the triple point on the fusion curve is uncertain. It was concluded that new and more refined experimental techniques would be necessary to determine this phase structure, and this will probably be taken up as a later project.

The rather outstanding success of the Simon equation in fitting the experimental data of not only indium and tin but also the Group VIII metals investigated by

---

[16] V. P. Butuzov and E. G. Ponyatovskii, Kristallografiya **1**, 736 (1956).

[17] V. P. Butuzov and M. G. Gonikberg, Doklady Akad. Nauk S.S.S.R. **91**, 1083 (1953) (English translation NSF-tr-144, December, 1953).

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, $V=15.7$ cm^3/g-atom for indium, and $\Delta E=70.0$ kcal/g-atom, $V=16.3$ cm^3/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 Salter[5] 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 constant[19] 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.