

V. CONCLUSION

The results of this paper yield a practical method of determining the lattice corrections to thermodynamic functions computed on the Thomas-Fermi model. No attempt has been made to take account of the long-range order which may be present in the amorphous phase above the fusion temperature. Presumably, the existence of such order must introduce corrections to thermodynamic functions computed on the Thomas-Fermi model, analogous to the lattice corrections.

Mott's theory of liquids³⁴ may provide an approach to such questions.

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³⁴ N. F. Mott, Proc. Roy. Soc. (London) A146, 465 (1934).

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Equation of the Fusion Curve*

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A generalization of the Lindemann law given previously is used in conjunction with the Murnaghan equation of state for a solid to derive a law of reduced states for fusion, valid for the case of classical excitation of the lattice vibrations at melting. If the bulk modulus and volume of the solid at fusion and the melting temperature are reduced by dividing the quantity in question by its corresponding value at the origin of the fusion curve, any reduced variable of this set can be expressed as a power of any other, with an exponent involving a constant appearing in the Murnaghan equation. It is shown that the ratio of the latent heat to the volume change of fusion obeys a similar law of reduced states, on the basis of an assumed form of the volume dependence of the Grüneisen parameter of the solid along the fusion curve. The constant appearing in the Murnaghan equation of state is interpreted physically in terms of an average Grüneisen parameter of the solid. The law of reduced states yields an immediate derivation of the empirical Simon equation for the fusion curve. For the alkali metals, it is shown that experimental values of the temperature exponent in the Simon equation are quantitatively compatible with the theoretical evaluation given, and, furthermore, that the theory can predict approximate values of the exponent, in practice.

THE empirical equation¹

$$\log(P_m + A) = B \log T_m + C, \quad (1)$$

where P_m and T_m are the fusion pressure and absolute temperature, respectively, and A , B , and C are disposable coefficients, has been proposed by Simon to represent the fusion curve. By evaluating the constant C at the triple point of temperature T_t (and negligible pressure), he has put the equation in the form

$$P_m = A[(T_m/T_t)^B - 1] \quad (2)$$

for elements of low melting point; this form will be referred to as the Simon equation. If a reduced pressure P_m' and temperature T_m' are defined by P_m/A and T_m/T_t , respectively, Eq. (2) yields the Simon law,

$$P_m' = T_m'^B - 1, \quad (3)$$

of corresponding states for fusion. This law is analogous to the law of corresponding states for a van der Waals gas, with the constant A and the triple-point temperature as reducing parameters corresponding to the critical pressure and temperature, respectively.

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¹ F. Simon, Z. Electrochem. 35, 618 (1929); Trans. Faraday Soc. 33, 65 (1937).

If the constants A and B are selected by trial, Eq. (2) yields a good fit to the observed melting curves of solids of low melting point. Values of the constants for various elements, as derived from experimental work prior to 1937, are tabulated (except for D_2)² by Ruhemann and Ruhemann.³ Later work⁴ has extended the pressure range over which the equation is applicable. The Simon exponent B is roughly 2 for most of the substances (He, H₂, Ne, N₂) of low melting point, except for A, for which it is somewhat over unity. For the alkali metals, T_t in Eq. (2) must be replaced by the normal melting temperature; reported values⁵ of the exponent B are approximately 4. Values quoted for the Simon exponent by different authors frequently are fairly discrepant for the same element. Part of the variance is presumably due to the fact that a requirement merely of fit to the data does not necessarily

² K. Clusius and E. Bartholomé, Z. physik. Chem. B30, 237 (1935).

³ M. Ruhemann and B. Ruhemann, *Low Temperature Physics* (Cambridge University Press, London, 1937), p. 97.

⁴ Holland, Huggill, Jones, and Simon, Nature 165, 147 (1950); Holland, Huggill, and Jones, Proc. Roy. Soc. (London) A207, 268 (1951); J. S. Dugdale and F. E. Simon, Proc. Roy. Soc. (London) A218, 291 (1953).

⁵ F. Simon and G. Glatzel, Z. anorg. u. allgem. Chem. 178, 309 (1929).