

respectively, and Eq. (9) becomes

$$\kappa_m = \kappa_{m,0} (T_m/T_{m,0})^{b'}, \quad (26)$$

where

$$b' = (6\gamma_{m,0} + 1) / [2(3\gamma_{m,0} - 1)]. \quad (27)$$

The three equations (25a) (25b), and (26) are valid only as osculating approximations at the origin; by means of Eq. (23), one can show that they differ only in the substitution of $\gamma_{m,0}$ for $\gamma_{m,Av}$ from their correspondents in the large, Eqs. (6), (8), and (9), respectively.

These osculating approximations are derivable directly from the Grüneisen postulate that the Debye frequency, in general, is a power-law function only of the volume; if ν_m is the Debye frequency of the solid at melting, this assumption yields the expression

$$\nu_m = G/V_m^{\gamma_{m,0}}, \quad (28)$$

where G is a constant, for ν_m in the neighborhood of the origin of the fusion curve. The Debye frequency of a monatomic solid at melting is given likewise by

$$\nu_m = s_m N^{1/3} M^{-1/2} \kappa_m^{1/2} V_m^{1/6}, \quad (29)$$

where M is the atomic weight, N is Avogadro's number, and s_m is a function, defined in I, of the value of Poisson's ratio of the solid at melting. On the assumption of I that the Poisson ratio at fusion is constant, comparison of Eqs. (28) and (29) yields Eq. (25a). Equation (25b) and thus Eq. (26) then follow directly from Eq. (7), or from the identification $\nu_m = \nu_L$, where ν_L is the Lindemann frequency defined in I.

II. SIMON EQUATION

The general result,

$$dP_m/dT_m = q\kappa_m/2(\gamma_m - \frac{1}{3})T_m, \quad (30)$$

for the slope of the fusion curve has been obtained in I. If q is given the constant value q_0 corresponding to the origin, integration of this equation with use of Eqs. (9) and (18) yields

$$P_m - P_{m,0} = (a/B)[(T_m/T_{m,0})^B - 1], \quad (31)$$

where $P_{m,0}$ is the pressure corresponding to the origin of the fusion curve, a is given by Eq. (17), and B is defined by Eq. (21). Equation (31) has precisely the form, with $A = a/B$, of the Simon equation (2) (except for the introduction of the constant $P_{m,0}$ of integration to make both sides of the equation vanish together at the origin). The equation assumes a reduced form, analogous to Eq. (20) for $L/\Delta V$, if the left-hand side is rewritten as $(P_m - P_{m,0})/a$.

Equation (31) of the fusion curve yields the correct initial slope demanded by Eq. (30), and the correct initial value a of the ratio $L/\Delta V$ required by Eq. (12); thus Clapeyron's equation is satisfied at the origin, independently of the value of the Simon exponent B . As has been pointed out, the parameter μ of Eq. (14),

which corresponds to the volume variation of $\gamma_m - \frac{1}{3}$ and enters B through β of Eq. (19), can be evaluated by application at the origin of Eq. (15) for d^2T_m/dP_m^2 . In this case, it follows that Eq. (31) yields the correct curvature of the fusion curve at the origin corresponding to Eq. (15); note, however, that this equation has been derived in I on the assumption that q is constant.

The derivation of Simon's equation given by Salter,¹⁴ based on the Debye equation of state, assumes that the Grüneisen parameter has a constant value. His result is essentially

$$P_m - P_{m,0} = A[(T_m/T_{m,0})^{b'} - 1], \quad (32)$$

where A is specified only as a constant and b' is defined by Eq. (27). Since the exponent b of Eq. (10) can be written in terms of the average Grüneisen parameter of Eq. (23) as

$$b = (6\gamma_{m,Av} + 1) / [2(\gamma_{m,Av} - 1)], \quad (33)$$

it follows that Salter's evaluation of the Simon exponent corresponds to substituting $\gamma_{m,0}$ for $\gamma_{m,Av}$ in b and taking $\beta = 0$ (corresponding to $\mu = 0$) in Eqs. (21) for B .

Equation (30) for dP_m/dT_m is susceptible to a physical interpretation. If one writes the parameter q , in a form deducible from results of I, as

$$q = (1 - \kappa_m \alpha_m dT_m/dP_m)^{-1}, \quad (34)$$

in which α_m is the coefficient of volume expansion of the solid at fusion, substitution of this expression into Eq. (30) yields

$$dP_m/dT_m = \kappa_m/2(\gamma_m - \frac{1}{3})T_m + \kappa_m \alpha_m. \quad (35)$$

The second term on the right-hand side of this equation is given by Grüneisen's law as

$$\kappa_m \alpha_m = \gamma_m C_{V,m} / V_m = [(\partial P / \partial T)_V]_m, \quad (36)$$

where $C_{V,m}$ is the heat capacity of the solid at fusion, and the subscript m on the last term designates evaluation of the partial derivative for the solid on the fusion curve. Hence, the second term in Eq. (35) for dP_m/dT_m corresponds to the increment in thermal pressure of the lattice as T_m is increased. Thus, the assumption $q = q_0$ made in deriving Eqs. (20) and (31) corresponds to the postulate that $[(\partial P / \partial T)_V]_m$ bear a constant ratio to the total derivative dP_m/dT_m along the melting curve. From the fact that

$$dP_m/dT_m = [(\partial P / \partial V)_T]_m dV_m/dT_m + [(\partial P / \partial T)_V]_m, \quad (37)$$

it follows that

$$[(\partial P / \partial V)_T]_m dV_m/dT_m = \kappa_m/2(\gamma_m - \frac{1}{3})T_m. \quad (38)$$

Hence, the first term in Eq. (35) for dP_m/dT_m corresponds to the increment, as T_m and thus V_m is changed, of that part of the pressure which depends directly on the volume, that is, the pressure corresponding (for low or moderate compression) to the potential energy of an atom in the interatomic force field. Salter's derivation

of the Simon constant; exponent obtain the to the Simon

Simon¹ is of the Approximate the evaluation be shown sion⁷ for theory of s

III.

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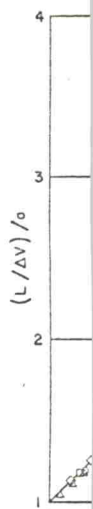


FIG. 1. Co for the ratio Bridgman's the Simon ex selected in ea

curves of the over pressure will be ignored made on a comparison values of available from and of q_0 if evaluated values of L values of γ I correspond The third e Equation when plot

¹⁷ P. W. Br
¹⁸ P. W. Br