expressions of $(\partial\gamma/\partial V)_T$ and $(\partial\gamma/\partial T)_V$,

$$\left(\frac{\partial\gamma}{\partial V}\right)_T = \frac{\gamma}{V} - \frac{\gamma}{C_V}\left(\frac{\partial C_V}{\partial V}\right)_T$$
$$+ \frac{1}{C_V K^2}\left[\left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K}\left(\frac{\partial K}{\partial P}\right)_T\right] \quad (15)$$

$$\left(\frac{\partial\gamma}{\partial T}\right)_V = \frac{V}{TC_V}\left(\frac{\partial C_V}{\partial V}\right)_T - \frac{\gamma}{C_V}\left(\frac{\partial C_V}{\partial T}\right)_V \quad (16)$$

which follow from equation (3), the first one by transforming $[\partial(\beta/K)/\partial V]_T$ into pressure derivatives at constant temperature, noting then that $(\partial\beta/\partial P)_T = -(\partial K/\partial T)_P$. In the vibrational formulation of the Mie–Grüneisen approximation, the resulting equations have the form

$$P + \frac{dW_L}{dV} = \frac{T\beta}{K}\frac{W_{\mathrm{vib}}}{TC_V} \quad (17)$$

$$-\frac{1}{K} + V\frac{d^2W_L}{dV^2}$$
$$= \frac{V\beta^2}{C_V^2 K^2}W_{\mathrm{vib}}\left[\frac{TC_V}{W_{\mathrm{vib}}} - 1 - \frac{T}{C_V}\left(\frac{\partial C_V}{\partial T}\right)_V\right]$$
$$+ \frac{W_{\mathrm{vib}}}{TC_V}\frac{T}{K^2}\left[\left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K}\left(\frac{\partial K}{\partial P}\right)_T\right]; \quad (18)$$

while in the thermal formulation they read

$$P + \frac{dW_C}{dV} = \frac{T\beta}{K}\frac{W_{\mathrm{th}}}{TC_V} \quad (19)$$

$$-\frac{1}{K} + V\frac{d^2W_C}{dV^2}$$
$$= \frac{V\beta^2}{C_V^2 K^2}W_{\mathrm{th}}\left[\frac{TC_V}{W_{\mathrm{th}}} - 1 - \frac{T}{C_V}\left(\frac{\partial C_V}{\partial T}\right)_V\right]$$
$$+ \frac{W_{\mathrm{th}}}{TC_V}\frac{T}{K^2}\left[\left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K}\left(\frac{\partial K}{\partial P}\right)_T\right]. \quad (20)$$

In the corresponding formulations of the Hildebrand approximation, they are instead:

$$P + \frac{dW_L}{dV} = \frac{T\beta}{K} \quad (21)$$

$$-\frac{1}{K} + V\frac{d^2W_L}{dV^2} = \frac{T}{K^2}\left[\left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K}\left(\frac{\partial K}{\partial P}\right)_T\right] \quad (22)$$

and

$$P + \frac{dW_C}{dV} = \frac{T\beta}{K} \quad (23)$$

$$-\frac{1}{K} + V\frac{d^2W_C}{dV^2} = \frac{T}{K^2}\left[\left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K}\left(\frac{\partial K}{\partial P}\right)_T\right]. \quad (24)$$

HUANG[4] assumed equations (17) and (19) as valid at all temperatures and attempted to investigate the validity of the Hildebrand approximation for a non-metal by searching for temperature ranges where equations (21) and (23) coincide with equations (17) and (19), respectively, computing the ratios W_{vib}/TC_V and W_{th}/TC_V by means of the Debye model. Clearly this procedure does not establish the relative merits of the Hildebrand and Mie–Grüneisen approximations. Thus HUANG's result that the ratio W_{vib}/TC_V approaches unity at temperatures somewhat above the Debye characteristic temperature, while the ratio W_{th}/TC_V approaches unity only at much higher temperatures, represents only a numerical verification for the Debye model of the general result to this effect which is apparent from the Thirring expansions for the vibrational and thermal energies. BORN and HUANG[5], on the other hand, have used equation (17) for the alkali halides at room temperature, adopting, however, an approximate expression for its volume derivative at constant temperature derived by neglecting the volume dependence of γ.

5. DISCUSSION OF THE RESULTS

A few definite statements on the validity of the Mie–Grüneisen and Hildebrand approximations to the equation of state of cubic solids under hydrostatic pressure are possible within the quasi-harmonic approximation. The thermal Mie–Grüneisen equation of state is correct for a non-metal in the T^3 region of the heat capacity, and the validity of the Debye model for the thermal thermodynamic functions in this region, which

implies that

$$\frac{TC_V}{W_{th}} = 1 + \frac{T}{C_V}\left(\frac{\partial C_V}{\partial T}\right)_V = 4,$$

ensures a welcome simplification of the form of this equation, and of its volume derivative at constant temperature. At temperatures somewhat above the Debye characteristic temperature $\Theta_2(V)$ for the (quasi-harmonic) heat capacity at high temperature, the appropriate equation of state is the vibrational Hildebrand equation, which has of course the advantage that its use, and that of its volume derivative, does not require the knowledge of the vibrational energy of the solid as a function of temperature and volume. At somewhat lower temperatures, the vibrational Mie–Grüneisen equation is the appropriate equation of state for solids in which γ is essentially a purely volume-dependent function at these temperatures; however, the use of this equation, and of its volume derivative, does require the knowledge of the vibrational energy of the solid $W_{vib}(V,T)$, and this has the Debye functional form with $\Theta_2(V)$ as the Debye characteristic temperature in the temperature region where its Thirring expansion can be truncated after the T^{-2} term (see Appendix). One may also add that the thermal Mie–Grüneisen and Hildebrand equations involve generally greater errors than the corresponding vibrational equations when used at the same temperature in the region of moderate temperatures. The various statements pertaining to moderately high temperatures can be assumed to apply to metals, as well as nonmetals, since at these temperatures the electronic terms in the vibrational thermodynamic functions of the solid are generally small compared to the lattice terms.

The applicability of these quasi-harmonic results to a particular solid depends naturally on the weight of the anharmonic contributions to its thermodynamic functions in the various ranges of temperature and volume. The available experimental evidence indicates that in the region of temperature around and below Θ_2 the anharmonic contributions to the thermal thermodynamic functions are quite small in a number of solids. Quite accurate evidence to this effect has been provided by BARRON et al.[21], who have shown

that the weight of the anharmonic contributions to the heat capacity at constant volume of various alkali halides at atmospheric pressure is still less than 1 per cent at temperatures around Θ_2. SALTER[16] has also pointed out that the entropy of copper and aluminum at atmospheric pressure remains apparently quasi-harmonic at least up to 300°K, since it has essentially the functional form $\ln(T/\Theta)$ in the temperature range from about 200°K to at least 300°K. An analogous test for sodium, using the data reported by MARTIN[22], reveals that the logarithmic functional form for the entropy at atmospheric pressure applies in the range extending roughly from 100°K to 200°K. On the other hand, an analysis of the available calculations of the anharmonic contributions to the vibrational thermodynamic functions, which concern simple force models of a linear chain of a face-centered cubic solid,[19] shows that the contributions to the vibrational free energy at temperatures around and somewhat below the appropriate Θs are at most comparable to the contributions to TC_V. Under these conditions, the characteristic temperature for the logarithmic term of the vibrational free energy is affected by the anharmonic terms only by a percentage comparable to their fractional weight in the heat capacity.

In the temperature range where the entropy of a solid has the functional form $\ln[T/\Theta(V)]$, γ must of course be a purely volume-dependent function, and one would actually expect γ not to vary significantly with temperature also at somewhat lower temperatures, where the following terms of the Stern expansion of the entropy are still small and a different volume dependence of the characteristic temperatures appropriate to the various terms of the expansion (see Appendix) is hardly detectable. These expectations are confirmed by the measurements of BIJL and PULLAN[23] which show that in copper and aluminum γ at atmospheric pressure does not vary with temperature in the range from 273°K to below 150°K. For sodium, one anticipates that γ at atmospheric pressure should not vary with temperature in the range extending roughly from 200°K to 100°K. An experimental verification of this prediction, when compared with the observation[24] that γ'' for sodium depends explicitly on temperature in this range, would provide also a verification of the quasi-harmonic theorem that γ'' approaches the