The temperature dependence of υ and $\mathcal{K}$ will be determined by considerations of thermodynamic consistency; dependence solely on temperature will be verified *a posteriori*.

Any valid equation of state, applicable for variable absolute temperature T, must conform to the thermodynamic identity

$$(\partial P/\partial T)_V = K\alpha, \tag{17}$$

where $K = -V(\partial P/\partial V)_T$ is the isothermal bulk modulus, and $\alpha = V^{-1}(\partial V/\partial T)_P$ is the volumetric coefficient of thermal expansion. Also, the equation must obey the relation

$$(\partial K/\partial T)_V = K'\alpha + K^2(\partial\alpha/\partial P)_T, \tag{18}$$

obtained by differentiation of Eq. (17), where

$$K' = -V(\partial K/\partial V)_T. \tag{19}$$

It is convenient to define a dimensionless parameter η by

$$\eta = -K\alpha^{-1}(\partial\alpha/\partial P)_T, \tag{20}$$

which ranges, numerically, from about 2 to perhaps 12 for different solids.[8] By virtue of the identity

$$K^{-1}(\partial K/\partial T)_P = K(\partial\alpha/\partial P)_T, \tag{21}$$

one can write Eq. (18) as

$$(\partial K/\partial T)_V = (K' - K\eta)\alpha. \tag{22}$$

The general forms (15) and (16) will be required to meet the conditions of the two identities (17) and (22). This procedure corresponds to requiring that

$$P = -(\partial F/\partial V)_T,$$

where F is the Helmholtz function, rather than

$$P = -dE/dV,$$

where E is the energy; note that $(\partial P/\partial T)_V$ in Eq. (17) equals $(\partial S/\partial V)_T$, where S is the entropy.

On the assumptions made, differentiation of Eqs. (15) and (16) with respect to temperature to obtain $(\partial P/\partial T)_V$ and $(\partial K/\partial T)_V$, respectively, and substitution of the results into Eqs. (17) and (22) yield two linear algebraic equations in $\partial \ln\upsilon/\partial T$ and $\partial \ln\mathcal{K}/\partial T$, whose solutions are

$$\partial \ln\upsilon/\partial T = \alpha[K^2 + P(K\eta - K')]/(K^2 - PK'), \tag{23a}$$

$$\partial \ln\mathcal{K}/\partial T = -\eta\alpha K^2/(K^2 - PK'). \tag{23b}$$

One notes that these equations imply that υ and $\mathcal{K}$ cannot depend solely on the temperature, as presupposed by the derivation [in the first instance, in the volume differentiation to obtain K of Eq. (16)]. It will be shown that, actually, υ and $\mathcal{K}$ are each a function only of temperature, to a certain approximation.

For most solids, P is considerably smaller than K up to relatively high pressures, although K and K' are comparable, in general. By means of the binomial

theorem, one can write Eq. (23a) to first order in the ratio P/K as

$$\partial \ln\upsilon/\partial T = \alpha(1 + \eta P/K). \tag{24}$$

Now, Birch has shown that the pressure dependence of $\alpha(T)$ at fixed temperature T is given approximately by[8]

$$\alpha = \alpha_0(1 - \eta_0 P/K), \tag{25}$$

where $\alpha_0(T)$ is the value of α at zero pressure and at temperature T, and $\eta_0(T)$ is the corresponding value of η. This equation is simply an approximate integral of the differential relation (20), but it agrees fairly well with Bridgman's experimental results on the change of thermal expansion (over the range 0–95°C) of the alkali metals with pressure up to the limit of measurement[8] (about 2×10^4 bars). Hence, to first order in the ratio P/K, Eq. (24) becomes

$$d \ln\upsilon/dT = \alpha_0(T), \tag{26}$$

where the right-hand side is a function of the temperature alone. The integral of this relation is

$$\upsilon = V_0 \exp\int_{T_0}^{T} \alpha_0 dT, \tag{27}$$

where V_0 is the initial volume corresponding to the temperature T_0 and zero pressure.

By a binomial expansion, Eq. (23b) can be expressed as

$$\partial \ln\mathcal{K}/\partial T = -\eta\alpha(1 + K'P/K^2) \tag{28}$$

to first order in P/K. The partial derivative of η with respect to pressure at constant temperature can be obtained as

$$\eta^{-1}(\partial\eta/\partial P)_T = (K\eta + K')/K^2 - (K/\eta\alpha)(\partial^2\alpha/\partial P^2)_T, \tag{29}$$

from the definition (20). In this equation, the second derivative appearing can be neglected consistently with the approximation (25) of Birch. In this case, use of Birch's result (25) and the analogous approximate integral of Eq. (29) yields

$$\partial \ln\mathcal{K}/\partial T = -\eta_0\alpha_0(1 + 2K'P/K^2), \tag{30}$$

from Eq. (28). One can reduce this relation approximately to

$$\partial \ln\mathcal{K}/\partial T = -\eta_0\alpha_0[1 + 2(n+m)P/K] \tag{31}$$

for P small, by replacing the ratio K'/K by its limiting value $n+m$ for normal volume, as obtained from Eq. (2). In contrast to the case with υ, it is seen that $\mathcal{K}$ can be dependent solely on temperature and the assumptions thus self-consistent, only in the limit $P \ll K$. Presupposing this limit, one can restrict the right-hand side of Eq. (31) to its leading term, and one obtains

$$\mathcal{K} = K_0 \exp\left[-\int_{T_0}^{T} \eta_0\alpha_0 dT\right], \tag{32}$$