

This assumption restricts E to the form,

$$E = C_V T + f(V) , \quad (\text{A.2})$$

where $f(V)$ is an arbitrary function of specific volume V .

Since C_V is constant, Maxwell's equations require

$$\left(\frac{\partial C_V}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V = 0 , \quad (\text{A.3})$$

which gives

$$P = r(V)T + y(V) = \frac{\Gamma C_V}{V} T - f'(V) . \quad (\text{A.4})$$

The assumption is made that

$$\left(\frac{\partial P}{\partial T} \right)_V = C_V \left(\frac{\partial P}{\partial E} \right)_V = \frac{\Gamma}{V} C_V = \text{constant} , \quad (\text{A.5})$$

where Γ is the Gruneisen parameter. Then, from Eqs. (A.4) and (A.5), we find that

$$r(V) = C_V \frac{\Gamma}{V} = b C_V = \text{constant} . \quad (\text{A.6})$$

Now any path on the thermodynamic equilibrium surface can be used to determine $y(V)$ in Eq. (A.4). Therefore, choosing the compression path along an isotherm is a logical choice because isothermal data are known in the form of the Murnaghan equation. Each phase is represented by

$$P(V_i) = B_{0i} \left[\left(\frac{V_i}{V_0} \right)^{-n_i} - 1 \right] , \quad (\text{A.7})$$

where the temperature T_0 is held constant, the subscript i indicates the particular phase, and the parameters B_{0i} and n_i are fitted constants. Combining Eqs. (A.4), (A.6), and (A.7) results in

$$P(V_i, T) = b C_{V_i} (T - T_0) + B_{0i} \left[\left(\frac{V_i}{V_0} \right)^{-n_i} - 1 \right], \quad (\text{A.8})$$

which defines any P, V, T path on the equilibrium surfaces.

To complete the definition of the surfaces, the function $f(V)$ of Eq. (A.2) has to be evaluated. This can be done in a consistent way with the use of the following identity:

$$G = E - T S + P V. \quad (\text{A.9})$$

The use of subscript i is dropped for convenience. To complete Eq. (A.9) an expression for S is required. Since

$$\left(\frac{\partial S}{\partial V} \right)_T = b C_V \quad (\text{A.10})$$

and

$$\left(\frac{\partial S}{\partial T} \right)_V = C_V / T. \quad (\text{A.11})$$

Then

$$S = S_0 - b C_V (V_0 - V) + C_V \ln(T/T_0). \quad (\text{A.12})$$