Specific heat at constant pressure and volume

Ref: Reif, Fundamentals of Statistical and Thermal Physics, p. 168

A general relation between C_P and C_V can be obtained this way. Taking (T, P) as independent variables (N or μ, if it is a valid thermodynamic variable, is implied, fixed, and of no concern here) we can write:

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \qquad (1)$$

Multiplying T and noting that $C = \frac{dQ}{dT} = T\frac{\partial S}{\partial T}$, this equation can be re-written as:

$$TdS = C_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP \qquad (2)$$

Changing independent variables from (T, P) to (T, V), we note:

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV \qquad (3)$$

In order to relate C_P and C_V, insert (3) to (2), consider the case $dV = 0$, and divide by dT:

$$C_V = C_P + T\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V \qquad (4)$$

From $dH = -SdT + VdP$, (H: enthalpy) we obtain a Maxwell's relation: $\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$. Thus,

$$C_V = C_P - T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V = C_P - TV\beta\left(\frac{\partial P}{\partial T}\right)_V \qquad (5)$$

$$C_P = C_V + TV\beta\left(\frac{\partial P}{\partial T}\right)_V \qquad (6)$$

where the thermal expansion coefficient $\beta \equiv \left(\frac{\partial V}{\partial T}\right)_P / V$.

Using Euler's chain rule $\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P / \left(\frac{\partial V}{\partial P}\right)_T$, and the bulk modulus $B \equiv -V\left(\frac{\partial P}{\partial V}\right)_T$, we get

$$\left(\frac{\partial P}{\partial T}\right)_V = \beta B \qquad (7)$$

$$C_P = C_V + TV\left(\frac{\partial P}{\partial T}\right)_V^2 / B \qquad (8)$$

$$C_P = C_V + TV\beta^2 B \qquad (9)$$

Another expression in terms of compressibility (inverse of bulk modulus) is of general interest. In terms of isothermal compressibility κ_T and adiabatic compressibility κ_S, the following holds:

$$C_P/C_V = \kappa_T/\kappa_S \qquad (10)$$

since $\kappa_S V \equiv -\left(\frac{\partial V}{\partial P}\right)_S = \left(\frac{\partial S}{\partial P}\right)_V / \left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V / \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P = \left(\frac{C_V}{C_P}\right)\left(-\frac{\partial V}{\partial P}\right)_T \equiv \frac{C_V}{C_P}\kappa_T V$.