Difference in Cp and Cv

From the definitions of Cp and Cv,

$$Cp - Cv = \left.\frac{dq}{dT}\right|_P - \left.\frac{dq}{dT}\right|_V \tag{1}$$

Substitution of the definition of entropy gives

$$Cp - Cv = T\left[\left.\frac{\partial S}{\partial T}\right|_P - \left.\frac{\partial S}{\partial T}\right|_V\right] \tag{2}$$

These partials are converted from the total differential obtained from $S = f(T,V)$

$dS = \left.\frac{\partial S}{\partial T}\right|_V dT + \left.\frac{\partial S}{\partial V}\right|_T dV$, which when divided by dT at dP = 0 becomes

$$\left.\frac{\partial S}{\partial T}\right|_P - \left.\frac{\partial S}{\partial T}\right|_V = \left.\frac{\partial S}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_P \tag{3}$$

Substituting Eq. (3) into Eq. (2) gives

$$Cp - Cv = T\left.\frac{\partial S}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_P \tag{4}$$

The Maxwell Relationship $\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V$ further transforms Eq. (4) to

$$Cp - Cv = T\left.\frac{\partial P}{\partial T}\right|_V \left.\frac{\partial V}{\partial T}\right|_P \tag{5}$$

The total differential from $P = (T,V)$ at dP = 0 gives $0 = \left.\frac{\partial P}{\partial V}\right)_T \left.\frac{\partial V}{\partial T}\right)_P + \left.\frac{\partial P}{\partial T}\right)_V$ and

$$\left.\frac{\partial P}{\partial T}\right|_V = -\left.\frac{\partial P}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_P = -\left.\frac{\partial V}{\partial T}\right|_P \Big/ \left.\frac{\partial V}{\partial P}\right|_T = \alpha/\beta \quad \text{where} \quad \alpha \equiv \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P \qquad \beta \equiv -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T$$

Therefore, Eq. (5) may be written

$$Cp - Cv = \frac{\alpha^2 TV}{\beta} \tag{6}$$

Note that substituting the definition of entropy into Eq. (1) does not introduce an additional constraint of reversibility since heat capacities are state functions.