

3.30 $C_p - C_V$: general relation

Starting from

$$dU = TdS - pdV \quad \text{i.e.} \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p \quad (3.74)$$

where we have used the corresponding Maxwell relation, we get

$$\begin{aligned} C_p - C_V &= \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial(U + pV)}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V \\ &= \left(\frac{(\frac{\partial U}{\partial T})_V \partial T + (\frac{\partial U}{\partial V})_T \partial V + p \partial V}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V \\ &= \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p \end{aligned} \quad (3.75)$$

Using the definitions of the thermal expansion coefficient and the isothermal compressibility and applying the chain rule we find

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p \quad \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T \quad \text{and} \quad \left(\frac{\partial p}{\partial T}\right)_V = -\frac{(\frac{\partial V}{\partial T})_p}{(\frac{\partial V}{\partial p})_T} = \frac{\alpha}{\kappa} \quad (3.76)$$

Including this in Eq. (3.75) we finally get

$$C_p - C_V = TV \frac{\alpha^2}{\kappa} \quad (3.77)$$