Beginning with the fundamental thermodynamic relation, and the definition of C_v,

$$\boldsymbol{TdS = dE + PdV - \mu dN, \quad C_v = T\left(\frac{\partial S}{\partial T}\right)_{N,V}}$$

derive the equality

$$\boldsymbol{\left(\frac{\partial C_v}{\partial V}\right)_{T,N} = T\left(\frac{\partial^2 P}{\partial T^2}\right)_{V,N}}$$

Solution:

Begin by finding $\left(\frac{\partial C_v}{\partial V}\right)_{T,N}$:

$$\left(\frac{\partial C_v}{\partial V}\right)_{T,N} = \frac{\partial}{\partial V}\left(T\left(\frac{\partial S}{\partial T}\right)_{N,V}\right) = T\left(\frac{\partial S}{\partial V \partial T}\right)_{N,T} \tag{1}$$

Now we need to find $\left(\frac{\partial S}{\partial V \partial T}\right)_{N,T}$, which can be done through the fundamental thermodynamic relation:

$$TdS = dE + PdV - \mu dN \tag{2}$$

$$TdS + SdT - SdT = dE + PdV - \mu dN \tag{3}$$

$$d(TS - E) = SdT + PdV - \mu dN \tag{4}$$

$$-dF = SdT + PdV - \mu dN \tag{5}$$

since F=E-TS. From (5), we find that

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \tag{6}$$

If we now take a partial derivative of S with respect to V and take a partial derivative of P with respect to T, we arrive at the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N} \tag{7}$$

If we now take a partial derivative with respect to T, we find

$$\left(\frac{\partial S}{\partial T \partial V}\right)_{T,N} = \left(\frac{\partial^2 P}{\partial T^2}\right)_{V,N} \tag{8}$$

Plugging this result into (1), we find

$$\left(\frac{\partial C_v}{\partial V}\right)_{T,N} = T\left(\frac{\partial S}{\partial V \partial T}\right)_{N,T} = T\left(\frac{\partial S}{\partial T \partial V}\right)_{N,T} = T\left(\frac{\partial^2 P}{\partial T^2}\right)_{V,N} \tag{9}$$

$$\left(\frac{\partial C_v}{\partial V}\right)_{T,N} = T\left(\frac{\partial^2 P}{\partial T^2}\right)_{V,N} \tag{10}$$

as claimed.