PS 20: Problem 2.27

The differentials of the thermodynamic potentials are

$$dF = -S dT - P dV \tag{1}$$

$$dG = -S dT + V dP \tag{2}$$

$$dH = T dS + V dP \tag{3}$$

The natural variables of (1) are

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V} \tag{4}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T} \tag{5}$$

Taking the partial derivative of (4) wrt V under constant T,

$$\left(\frac{\partial S}{\partial V}\right)_{T} = -\frac{\partial}{\partial V} \left[\left(\frac{\partial F}{\partial T}\right)_{V} \right]_{T}
= -\frac{\partial}{\partial T} \left[\left(\frac{\partial F}{\partial V}\right)_{T} \right]_{V}
\left[\left(\frac{\partial S}{\partial V}\right)_{T} = \left(\frac{\partial P}{\partial T}\right)_{V} \right]$$
(6)

The natural variables of (2) are

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P} \tag{7}$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T \tag{8}$$

Taking the partial derivative of (7) wrt P under constant T,

$$\left(\frac{\partial S}{\partial P}\right)_{T} = -\frac{\partial}{\partial P} \left[\left(\frac{\partial G}{\partial T}\right)_{P} \right]_{T}
= -\frac{\partial}{\partial T} \left[\left(\frac{\partial G}{\partial P}\right)_{T} \right]_{P}
\left[\left(\frac{\partial S}{\partial P}\right)_{T} = -\left(\frac{\partial V}{\partial T}\right)_{P} \right]$$
(9)

The natural variables of (3) are

$$T = \left(\frac{\partial H}{\partial S}\right)_P \tag{10}$$

$$V = \left(\frac{\partial H}{\partial P}\right)_{S} \tag{11}$$

Taking the partial derivative of (10) wrt P under constant S,

$$\left(\frac{\partial T}{\partial P}\right)_{S} = \frac{\partial}{\partial P} \left[\left(\frac{\partial H}{\partial S}\right)_{P} \right]_{S}$$

$$= \frac{\partial}{\partial S} \left[\left(\frac{\partial H}{\partial P}\right)_{S} \right]_{P}$$

$$\left[\left(\frac{\partial T}{\partial P}\right)_{S} = \left(\frac{\partial V}{\partial S}\right)_{P} \right]$$
(12)