1. Starting from:

$$dH = T\,dS + V\,dP$$

Show that:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

Take $\left(\frac{\partial}{\partial P}\right)_T$ of both sides:

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

Recognize Maxwell relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ and substitute

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

2. Suppose the internal energy U is a function of temperature T and volume V

(a) Starting from:

$$U = A + TS$$

Show that:

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$$

$$dU = dA + T\,dS + S\,dT$$

Take $\left(\frac{\partial}{\partial V}\right)_T$ of both sides:

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial A}{\partial V}\right)_T + T\left(\frac{\partial S}{\partial V}\right)_T$$

Recognize two Maxwell relations:

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Substitute back:

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$$

(b) Use your result to show that internal energy has no volume dependence for an ideal gas, but for real gases internal energy can have volume dependance.

$$PV = nRT \implies \left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{nRT}{V}\right) = \frac{nR}{V} = \frac{P}{T}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{P}{T}\right) = 0$$

But this does not hold for non ideal gases, since $P \neq \frac{nRT}{V}$, so $\left(\frac{\partial P}{\partial T}\right)_V \neq \frac{P}{T}$

3. Starting from:

$$dU = TdS - PdV$$

Show that:

$$\left(\frac{\partial U}{\partial S}\right)_T = -P^2\left(\frac{\partial (T/P)}{\partial P}\right)_V$$

Take $\left(\frac{\partial}{\partial S}\right)_T$ of both sides and use Use Maxwell $\left(\frac{\partial V}{\partial S}\right)_T = \left(\frac{\partial T}{\partial P}\right)_V$:

$$\begin{aligned}\left(\frac{\partial U}{\partial S}\right)_T &= T\left(\frac{\partial S}{\partial S}\right)_V - P\left(\frac{\partial V}{\partial S}\right)_T \\ &= T - P\left(\frac{\partial T}{\partial P}\right)_V\end{aligned}$$

Work backwards from result:

$$\begin{aligned}\frac{\partial}{\partial P}\left(\frac{T}{P}\right)_V &= \frac{1}{P}\left(\frac{\partial T}{\partial P}\right)_V - \frac{T}{P^2} \\ -P^2\left(\frac{\partial (T/P)}{\partial P}\right)_V &= -P^2\left[\frac{1}{P}\left(\frac{\partial T}{\partial P}\right)_V - \frac{T}{P^2}\right] \\ &= T - P\left(\frac{\partial T}{\partial P}\right)_V = \left(\frac{\partial U}{\partial S}\right)_T\end{aligned}$$

Homework Problem 20

1. Starting from:

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

Show that:

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$