Exercise 2.4

This is completely analogous with the derivation for C_p, but with enthalpy in the place on energy.

We start off with an aside, which we'll use later:

$$\left(\frac{\partial H}{\partial S}\right)_{p,n} = \left(\frac{\partial T}{\partial S}\right)_{p,n} = \frac{T}{C_p} \tag{1}$$

Knowing that, we basically follow the same argument that Chandler makes on page 34.

The first-order fluctuations vanish in equilibrium systems. So we approximate the second-order fluctuations of the enthalpy in terms of entropy. That gives us:

$$\begin{align}
\delta^2 H &= (\delta^2 H)^{(1)} + (\delta^2 H)^{(2)} \tag{2}\\
&= \frac{1}{2}\left(\frac{\partial^2 H}{\partial S^2}\right)^{(1)}_{p,n} (\delta S^{(1)})^2 + \frac{1}{2}\left(\frac{\partial^2 H}{\partial S^2}\right)^{(2)}_{p,n} (\delta S^{(2)})^2 \tag{3}\\
&= \frac{1}{2}\left(\delta S^{(1)}\right)^2 \left(\left(\frac{\partial^2 H}{\partial S^2}\right)^{(1)}_{p,n} + \left(\frac{\partial^2 H}{\partial S^2}\right)^{(2)}_{p,n}\right) \tag{4}
\end{align}$$

where the last equation uses the fact that $\delta S^{(1)} = -\delta S^{(2)}$. Now we insert Eq. (1) and obtain

$$\begin{align}
\left(\delta^2 H\right)_{S,p,n} &= \frac{1}{2}\left(\delta S^{(1)}\right)^2 \left(\frac{T^{(1)}}{C_p^{(1)}} + \frac{T^{(2)}}{C_p^{(2)}}\right) \tag{5}\\
&= \frac{1}{2}\left(\delta S^{(1)}\right)^2 T \left(\frac{1}{C_p^{(1)}} + \frac{1}{C_p^{(2)}}\right) \tag{6}
\end{align}$$

Since stability requires that $\delta^2 H \geq 0$, and we have $(\delta S^{(1)})^2 \geq 0$, that leaves us with

$$T\left(\frac{1}{C_p^{(1)}} + \frac{1}{C_p^{(2)}}\right) \geq 0 \tag{7}$$

As Chandler notes, this must be true for any partitioning of the system, including the case that one partition is infinitesimally small. That gives us

$$\frac{T}{C_p} \geq 0 \tag{8}$$

which means that the temperature and the constant pressure heat capacity must have the same sign. Since temperature is generally positive, that gives us $C_p \geq 0$.