Exercise 2.7

First, see the document I wrote up when I was taking this class as a grad student: "On the Small Changes in Auxiliary Functions Near Equilibrium." That document repeats the arguments Chandler presents on pages 35-36, and generalizes them to arbitrary order.

From there, we just need to remember the definition of pressure in terms of the Helmholtz free energy A:

$$\frac{\partial A}{\partial V} = -p \tag{1}$$

This means that for any order derivative of A with respect to V, we have:

$$\frac{\partial^n A}{\partial V^n} = -\frac{\partial^{n-1} p}{\partial V^{n-1}} \tag{2}$$

So now let's look at the two specific cases posed in this problem. In each case, we'll translate the derivatives of the pressure into derivatives of the Helmholtz free energy:

1. Rephrase the question: if we know that

   $$\frac{\partial p}{\partial V} = -\frac{\partial^2 A}{\partial V^2} = 0 \tag{3}$$

   then what can we say about:

   $$\frac{\partial^3 p}{\partial V^3} = -\frac{\partial^4 A}{\partial V^4} \tag{4}$$

   The first thing to notice here is that we skipped $\partial^3 A / \partial V^3$. That is because, as mentioned in my companion document, all odd-order derivatives must be zero. So if $\partial p / \partial V$ is zero, then the third derivative of pressure (fourth of free energy) is the first that contributes. As discussed in the accompanying document, our ability to arbitrarily divide the system means that if the sum of the derivatives for the divided system must be positive, then so must each derivative individually. Since the even derivatives of the free energy have to be positive, we obtain:

   $$\frac{\partial^3 p}{\partial V^3} < 0 \tag{5}$$

2. In the second part, we're asked if that third derivative is zero, what is known about the fourth derivative. We solve this quickly by translating the derivatives to the Helmholtz free energy:

   $$\frac{\partial^4 p}{\partial V^4} = -\frac{\partial^5 A}{\partial V^5} \tag{6}$$

   As discussed in the accompanying document, the odd derivatives of the Helmholtz free energy have to be zero. Therefore, so do the even derivatives of the pressure with repect to volume.