Tips for Solving Question 1 from Assignment

Given this relation

$$\left(\frac{\partial z}{\partial p}\right)_T = \left(\frac{\partial z}{\partial v}\right)_T \left(\frac{\partial v}{\partial p}\right)_T = \frac{\left(\frac{\partial z}{\partial v}\right)_T}{\left(\frac{\partial p}{\partial v}\right)_T}$$

$$\left(\frac{\partial^2 f}{\partial p^2}\right)_T = \left(\frac{\partial^2 z}{\partial v^2}\right)_T \left(\frac{\partial v}{\partial p}\right)_T^2 + \left(\frac{\partial z}{\partial v}\right)_T \left(\frac{\partial^2 v}{\partial p^2}\right)_T$$

Consider f = z, then

$$\left(\frac{\partial^2 z}{\partial p^2}\right)_T = \left(\frac{\partial^2 z}{\partial v^2}\right)_T \left(\frac{\partial v}{\partial p}\right)_T^2 + \left(\frac{\partial z}{\partial v}\right)_T \left(\frac{\partial^2 v}{\partial p^2}\right)_T$$

Separate in two parts A +B for example and then take the derivative w.r.t p

$$z(v,T) = \frac{p(v,T)v}{RT}$$

Consider a function g(v,T)

Key Tip

Remember that $\frac{\partial}{\partial p}\left(\frac{\partial^n z}{\partial v^n}\right)_T = \left(\frac{\partial^{n+1} z}{\partial v^{n+1}}\right)_T \left(\frac{\partial v}{\partial p}\right)_T$ due to the chain rule.

Equation (2)

Equation (2): Third Derivative of v with respect to p

1. **Start from identity**:

$$1 = \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial p}\right)_T$$

Remember: p depends on v

First derivative:

$$0 = \left(\frac{\partial^2 p}{\partial v^2}\right)_T \left(\frac{\partial v}{\partial p}\right)_T^2 + \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial^2 v}{\partial p^2}\right)_T$$

Take another derivative, separate the terms in A and B. You should get something like:

$$\left(\frac{\partial^3 p}{\partial v^3}\right)_T \left(\frac{\partial v}{\partial p}\right)_T^3 + 3\left(\frac{\partial^2 p}{\partial v^2}\right)_T \left(\frac{\partial v}{\partial p}\right)_T \left(\frac{\partial^2 v}{\partial p^2}\right)_T + \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial^3 v}{\partial p^3}\right)_T = 0$$

Use the known expression for $\left(\frac{\partial^2 v}{\partial p^2}\right)_T = -\left(\frac{\partial^2 p}{\partial v^2}\right)_T \left(\frac{\partial p}{\partial v}\right)_T^{-3}$ to simplify.

Equation (3)

1. **Start with Equation (1)**:

$$\left(\frac{\partial^3 z}{\partial p^3}\right)_T = \text{Eq. } (1)$$

2. **Substitute known relationships**:

- $\left(\frac{\partial v}{\partial p}\right)_T = \left(\frac{\partial p}{\partial v}\right)_T^{-1}$
- $\left(\frac{\partial^2 v}{\partial p^2}\right)_T = -\left(\frac{\partial^2 p}{\partial v^2}\right)_T \left(\frac{\partial p}{\partial v}\right)_T^{-3}$
- $\left(\frac{\partial^3 v}{\partial p^3}\right)_T$ from Equation (2)

Simplify and that is it.

Question 2

Step 1: Express heat capacities in terms of entropy

The molar heat capacities can be written as:

$$c_{p,m} = T\left(\frac{\partial s}{\partial T}\right)_p, \qquad c_{v,m} = T\left(\frac{\partial s}{\partial T}\right)_v.$$

Step 2: Relate the entropy derivatives using the cyclic rule

Using the multivariable chain rule:

$$\left(\frac{\partial s}{\partial T}\right)_p = \left(\frac{\partial s}{\partial T}\right)_v + \left(\frac{\partial s}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p.$$

Step 3: Use a Maxwell relation to simplify

From the Helmholtz free energy $a = u - Ts$, we have:

$$da = -s\,dT - p\,dv.$$

Exact differential . The mixed part of derivatives must be equal.

$$\left(\frac{\partial}{\partial v}\left(\frac{\partial a}{\partial T}\right)_v\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial a}{\partial v}\right)_T\right)_v$$

Using PV = nRT you should get the result.