

# Tips for Solving Question 1 from Assignment

Given this relation

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

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

Consider a  
function  $g(v, T)$

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

## 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:

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

## 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.