CHEM 3PC3

Assignment 1

October 22, 2025

Name: ______________________________

Student Number: ______________________________

SUBMISSION INSTRUCTIONS — READ CAREFULLY

To receive full credit, you must follow these steps:

1. Answer all the questions.
2. Write your solutions on new, separate pages. Do not write your solutions in the margins of this paper.
3. At the top of each solution page, clearly write the corresponding question number (e.g., **"Question 5"**). If you use more than one page for a question, write the question number on each page (e.g., **"Question 5 (Page 1 of 2)"**).
4. **If you cannot solve a question, still attach a page with the question number and write "Blank" or "No Answer"** to indicate you attempted it.
5. **If you are unsure of a complete answer, still attempt the question:** attach a page with the question number and write down any relevant thoughts, formulas, or initial steps. Partial credit may be awarded for demonstrated effort and correct reasoning, whereas a blank answer will receive no credit.
6. Show all your work clearly and legibly. Unorganized or illegible work may not receive credit.

1 Problems

1. The compressibility is defined as,

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

where p is the pressure, v is the molar volume, R is the ideal gas constant, and T is the absolute temperature. A simple approximation is to use the fact the ideal gas law is exact at zero pressure

$$z(p=0,T) = 1.$$

and then approximate $z(p,T)$ as a Taylor series,

$$z(p,T) = 1+p\left(\frac{\partial z(p=0,T)}{\partial p}\right)_T + \frac{p^2}{2}\left(\frac{\partial^2 z(p=0,T)}{\partial p^2}\right)_T + \frac{p^3}{3!}\left(\frac{\partial z(p=0,T)}{\partial p}\right)_T + \cdots \quad (1)$$

To derive this expression from gas law, one uses Faa di Bruno's formulas, which are the generalization of the inverse-function theorem to higher-order derivatives.

The first derivative can be evaluated using

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

The second derivative gives,

$$\begin{aligned}\left(\frac{\partial^2 z}{\partial p^2}\right)_T &= \left[\left(\frac{\partial^2 z}{\partial p \partial v}\right)_T\right] \left(\frac{\partial v}{\partial p}\right)_T + \left(\frac{\partial z}{\partial v}\right)_T \left(\frac{\partial^2 v}{\partial p^2}\right)_T \\ &= \left[\left(\frac{\partial^2 z}{\partial v \partial v}\right)_T \left(\frac{\partial v}{\partial p}\right)_T\right] \left(\frac{\partial v}{\partial p}\right)_T + \left(\frac{\partial z}{\partial v}\right)_T \left(\frac{\partial^2 v}{\partial p^2}\right)_T \\ &= \left(\frac{\partial^2 z}{\partial v^2}\right)_T \left(\frac{\partial v}{\partial p}\right)_T^2 + \left(\frac{\partial z}{\partial v}\right)_T \left(\frac{\partial^2 v}{\partial p^2}\right)_T \\ &= \frac{\left(\frac{\partial^2 z}{\partial v^2}\right)_T}{\left(\frac{\partial p}{\partial v}\right)_T^2} + \left(\frac{\partial z}{\partial v}\right)_T \left(\frac{\partial^2 v}{\partial p^2}\right)_T\end{aligned}$$

The equation on the third line is the conventional form of the chain rule for second derivatives. Simplify the last expression, we need the inverse function theorem for second derivatives, which is a corollary to Faà di Bruno's formulas.

To simplify the last expression, we need the inverse function theorem for second derivatives, which is a corollary to Faà di Bruno's formulas. Use the standard chain rule

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

but assume that $f = z$. Then,

$$\begin{aligned}\left(\frac{\partial^2 p}{\partial v^2}\right)_T &= \left(\frac{\partial^2 p}{\partial v^2}\right)_T \left(\frac{\partial v}{\partial p}\right)_T^2 + \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial^2 v}{\partial p^2}\right)_T \\ 0 &= \left(\frac{\partial^2 p}{\partial v^2}\right)_T \left(\frac{\partial v}{\partial p}\right)_T^2 + \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial^2 v}{\partial p^2}\right)_T \\ \left(\frac{\partial^2 v}{\partial p^2}\right)_T &= -\left(\frac{\partial^2 p}{\partial v^2}\right)_T \left(\frac{\partial p}{\partial v}\right)_T^{-3}\end{aligned}$$

Substituting this expression into the final equation, one has

$$\left(\frac{\partial^2 z}{\partial p^2}\right)_T = \left[\left(\frac{\partial^2 z}{\partial v^2}\right)_T \left(\frac{\partial p}{\partial v}\right)_T - \left(\frac{\partial z}{\partial v}\right)_T \left(\frac{\partial^2 p}{\partial v^2}\right)_T\right] \left(\frac{\partial p}{\partial v}\right)_T^{-3}$$

The third-derivative expressions are

$$\left(\frac{\partial^3 z}{\partial p^3}\right)_T = \left(\frac{\partial^3 z}{\partial v^3}\right)_T \left(\frac{\partial v}{\partial p}\right)_T^3 + 3\left(\frac{\partial^2 z}{\partial v^2}\right)_T \left(\frac{\partial^2 v}{\partial p^2}\right)_T \left(\frac{\partial v}{\partial p}\right)_T + \left(\frac{\partial z}{\partial v}\right)_T \left(\frac{\partial^3 v}{\partial p^3}\right)_T \tag{1}$$

$$\left(\frac{\partial^3 v}{\partial p^3}\right)_T = 3\left(\frac{\partial^2 p}{\partial v^2}\right)_T^2 \left(\frac{\partial p}{\partial v}\right)_T^{-5} - \left(\frac{\partial^3 p}{\partial v^3}\right)_T \left(\frac{\partial p}{\partial v}\right)_T^{-4} \tag{2}$$

$$\left(\frac{\partial^3 z}{\partial p^3}\right)_T = \left(\frac{\partial^3 z}{\partial v^3}\right)_T \left(\frac{\partial p}{\partial v}\right)_T^{-3} - 3\left(\frac{\partial^2 z}{\partial v^2}\right)_T \left(\frac{\partial^2 p}{\partial v^2}\right)_T \left(\frac{\partial p}{\partial v}\right)_T^{-4} - \left(\frac{\partial z}{\partial v}\right)_T \left(\frac{\partial^3 p}{\partial v^3}\right)_T \left(\frac{\partial p}{\partial v}\right)_T^{-4} + 3\left(\frac{\partial z}{\partial v}\right)_T \left(\frac{\partial^2 p}{\partial v^2}\right)_T^2 \left(\frac{\partial p}{\partial v}\right)_T^{-5} \tag{3}$$

Obtain equations (1), (2) and (3).

Hints: To find Equation (1):

1. **Start from the second derivative:**

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

where

$$A = \left(\frac{\partial^2 z}{\partial v^2}\right)_T \left(\frac{\partial v}{\partial p}\right)_T^2, \qquad B = \left(\frac{\partial z}{\partial v}\right)_T \left(\frac{\partial^2 v}{\partial p^2}\right)_T$$

2. **Differentiate A and B:**

$$\frac{\partial A}{\partial p}, \quad \frac{\partial B}{\partial p}$$

Remember:

$$\frac{\partial}{\partial p}\left(\frac{\partial^n z}{\partial v^n}\right)_T = \left(\frac{\partial^{n+1} z}{\partial v^{n+1}}\right)_T \left(\frac{\partial v}{\partial p}\right)_T$$

(from the chain rule).

3. **To find Equation (2):**

   (a) **Start from the identity:**

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

   (b) **Take the first derivative:**

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

   (c) **Define helper terms:**

$$\alpha = \left(\frac{\partial^2 p}{\partial v^2}\right)_T \left(\frac{\partial v}{\partial p}\right)_T^2, \qquad \beta = \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial^2 v}{\partial p^2}\right)_T$$

   Then differentiate α and β again to obtain $\left(\frac{\partial^3 v}{\partial p^3}\right)_T$.

4. **To find Equation (3):**

   (a) **Start from Equation (1):**

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

(b) **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)

2. Show that for an ideal gas, the difference between the molar constant-pressure heat capacity and the molar constant-volume heat capacity is equal to the ideal gas constant,

$$c_{p,m} - c_{v,m} = R,$$

where $c_{p,m}$ is the molar heat capacity at constant pressure and $c_{v,m}$ is the molar heat capacity at constant volume.

1. Hint: Use the cyclic relation among thermodynamic variables.
2. Relate the entropy derivatives using the cyclic rule using the multivariable chain rule:

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

3. The Redlich–Kwong equation of state is given by:

$$P_{RK}(V,T) = \frac{RT}{V-b} - \frac{a}{\sqrt{T}\,V(V+b)},$$

where R, a and b are constants.

Derive the analytical expression of the integral,

$$\int V \left(\frac{\partial P_{RK}(V,T)}{\partial V}\right)_T dV.$$