1. By examining variations in $E$, $F$, $H$ and $G$, derive the four different Maxwell relations for the partial derivatives of $S, p, T$ and $V$.

ii. Obtain the partial derivative identity

$$\frac{\partial S}{\partial T}|_p = \frac{\partial S}{\partial T}|_V + \frac{\partial S}{\partial V}|_T \frac{\partial V}{\partial T}|_p$$

iii. Obtain the partial derivative identity

$$\frac{\partial p}{\partial T}|_V \frac{\partial T}{\partial V}|_p \frac{\partial V}{\partial p}|_T = -1$$

2. Consider a gas with a fixed number of molecules. Two experimentally accessible quantities are $C_V$, the heat capacity at fixed volume and $C_p$, the heat capacity at fixed pressure, defined as

$$C_V = T \frac{\partial S}{\partial T}|_V, \quad C_p = T \frac{\partial S}{\partial T}|_p$$

Using the results of the previous question, show that:

i. $C_p - C_V = T \frac{\partial V}{\partial T}|_p \frac{\partial p}{\partial T}|_V = -T \frac{\partial V}{\partial T}|_p \frac{\partial p}{\partial V}|_T$

ii. $\frac{\partial E}{\partial V}|_T = T \frac{\partial p}{\partial T}|_V - p$

iii. $\frac{\partial E}{\partial p}|_T = -T \frac{\partial V}{\partial T}|_p - p \frac{\partial V}{\partial p}|_T$

iv. $\frac{\partial C_V}{\partial V}|_T = T \frac{\partial^2 p}{\partial T^2}|_V$

v. $\frac{\partial C_p}{\partial p}|_T = -T \frac{\partial^2 V}{\partial T^2}|_p$
3. Consider a classical ideal gas with equation of state \( pV = Nk_B T \) and constant heat capacity \( C_V = Nk_B \alpha \) for some \( \alpha \). Use the results above to show that \( C_p = Nk_B(\alpha + 1) \), and that the entropy is

\[
S = Nk_B \log \left( \frac{V}{N} \right) + Nk_B \alpha \log T + \text{const}.
\]

Deduce that, for an adiabatic process (with \( dS = 0 \)), \( VT^\alpha \) is constant and, equivalently, \( pV^\gamma \) is constant, where \( \gamma = C_p/C_V \).

4. This question describes the Joule-Thomson process (also known as the Joule-Kelvin process). The figure shows a thermally insulated pipe which has a porous barrier separating two halves of the pipe. A gas of volume \( V_1 \), initially on the left-hand side of the pipe, is forced by a piston to go through the porous barrier using a constant pressure \( p_1 \). Assume the process can be treated quasistatically. As a result the gas flows to the right-hand side, resisted by another piston which applies a constant pressure \( p_2 \) (\( p_2 < p_1 \)). Eventually all of the gas occupies a volume \( V_2 \) on the right-hand side.

\[\begin{array}{cc}
\text{Before} & \text{After} \\
\begin{array}{c}
P_1 \\
V_1 \\
P_2 \\
\end{array} & \begin{array}{c}
P_1 \\
V_2 \\
P_2 \\
\end{array} \\
\end{array}\]

**Key:** insulated pipe, porous barrier, sliding pistons

i. Show that enthalpy, \( H = E + pV \), is conserved.

ii. Find the Joule-Thomson coefficient \( \mu_{JT} \equiv \left( \frac{\partial T}{\partial p} \right)_H \) in terms of \( T, V, \) the heat capacity at constant pressure \( C_p \), and the volume coefficient of expansion \( \alpha \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \). (Hint: You will need to use a Maxwell relation).

iii. What is \( \mu_{JT} \) for an ideal gas?

iv. If we wish to use the Joule-Thomson process to cool a real (non-ideal) gas, what must the sign of \( \mu_{JT} \) be?

v. Derive \( \mu_{JT} \) for a gas obeying the van der Waals equation of state to leading order in the density \( N/V \). For what values of temperature \( T \) can the gas be cooled?
5. A (non-ideal) gas has constant heat capacities $C_V$ and $C_p$. Using the results of Question 2, show that its equation of state can be written as

$$(C_p - C_V)T = (p + a)(V + b)$$

where $a$ and $b$ are constants. Show also that $E$ is of the form $E = C_V T + f(V)$, find $f(V)$ and calculate the entropy as a function of $V$ and $T$.

6. The Dieterici equation of state for a gas is

$$p = \frac{k_B T}{v - b} \exp \left( -\frac{a}{k_B T v} \right)$$

where $v = V/N$. Find the critical point and compute the ratio $p_c v_c / k_B T_c$. Calculate the critical exponents $\beta$, $\delta$ and $\gamma$.

7. The $q$-state Potts model is a generalisation of the Ising model. At each lattice site lives a variable $\sigma_i \in \{1, 2, \ldots, q\}$. The Hamiltonian is given by the sum over nearest neighbors

$$H_{\text{Potts}} = -\frac{3J}{2} \sum_{\langle ij \rangle} \delta_{\sigma_i \sigma_j}$$

How many ground states does the system have at $T = 0$?

Show that the 3-state Potts model is equivalent to the Hamiltonian

$$H = -J \sum_{\langle ij \rangle} \vec{s}_i \cdot \vec{s}_j$$

where $\vec{s}_i$ take values in the set

$$\vec{s}_i \in \left\{ \left( \begin{array}{c} 1 \\ 0 \end{array} \right), \left( \begin{array}{c} -1/2 \\ \sqrt{3}/2 \end{array} \right), \left( \begin{array}{c} -1/2 \\ -\sqrt{3}/2 \end{array} \right) \right\}$$

By developing a mean field theory for $H$ determine the self-consistency requirement for the magnetisation $\vec{m} = \langle \vec{s}_i \rangle$. Compute the mean field free energy and show that theory undergoes a first order phase transition even in the absence of an external field.

[Hint: This calculation will be simpler if you argue that you can focus on magnetisation vectors of the form $\vec{m} = (m, 0)$.]

8. Consider the free energy

$$F = a(T)m^2 + b(T)m^4 + c(T)m^6$$
where $b(T) < 0$ and, for stability, $c(T) > 0$ for all $T$. Sketch the possible behaviours of the free energy as $a(T)$ varies and, in each case, identify the ground state and metastable states. Show that the system undergoes a first order phase transition at some temperature $T_c$. Determine the value $a(T_c)$ and the discontinuity in $m$ at the transition.