Question 1:

Consider a closed system at constant volume composed of a very large number N of distinguishable subsystem which do not interact with each other upon forming the larger system. The subsystem can be only be in one of two energy states: $E = 0$, or $E = \varepsilon$.

a) What is the maximum possible value of the energy per subsystem ($E_{\text{max}}/N$) when the system is in equilibrium (at any thermodynamic condition)?

b) In this condition of maximum energy, what is the entropy of the systems ($S_{\text{tot}}/N$)?

c) Sketch the heat capacity of the system as function of temperature. Pay particular attention to limiting values (e.g. what is the value of the heat capacity at $T = 0$ and how is that value approached; value at high temperature, etc.)

\[ a) \quad p_0 = \frac{p}{\varepsilon} = \frac{1}{2} \rightarrow \text{high-T limit} \Rightarrow E_{\text{max}}/N = \varepsilon/2 \]

\[ b) \quad \text{Entropy per subsystem} = k_B \ln 2 \rightarrow S_{\text{tot}}/N = k_B \ln 2 \]

or think of $S = (N \ln 2) / N$ for total system

\[ S = \frac{N!}{N^N \cdot N!} = N \ln N - N \ln N - \frac{N}{2} \ln N - \frac{N}{3} \ln N + \frac{N}{2} + \frac{N}{3} \]

\[ = N \left[ \ln N - \ln N \right] = N \ln 2 \]

\[ S_{\text{tot}}/N = k_B \ln 2 \]

\[ c) \quad \text{Sketch heat capacity} \]

\[ \text{Entropy vs. temperature} \]
(b) \[ V_1 = 1 \text{L} = 10^{-3} \text{m}^3 \]
\[ T_1 = 800 \text{K} \]
\[ \Rightarrow P_1 = \frac{nRT_1}{V_1} = \frac{1 \times 8.314 \times 800}{10^{-3}} = 6.69 \times 10^6 \text{Pa} = 66 \text{atm} \]

\[ V_2 = 2 \text{L} = 2 \times 10^{-3} \text{m}^3 \]
\[ T_2 = 800 \text{K} \]
\[ \Rightarrow P_2 = \frac{nRT_2}{V_2} = \frac{1 \times 8.314 \times 800}{2 \times 10^{-3}} = 3.34 \times 10^6 \text{Pa} = 33 \text{atm} \]

\[ V_3 = 1 \text{L} = 1 \times 10^{-3} \text{m}^3 \]
\[ T_3 = ? \]
\[ P_3 = ? \]

For \(2 \rightarrow 3\), the path is adiabatic

\[ dU = \delta Q + \delta W = \delta W \Rightarrow dU = -PdV = 0 \]

For an ideal gas, \( dU = nC_v dT \)
\[ \Rightarrow nC_v dT = -PdV \]
\[ \Rightarrow nC_v dT = -\frac{nRT}{V} dV \]
\[
\frac{C_v}{k} \frac{dT}{T} = -\frac{dV}{V}
\]

\[\Rightarrow \frac{C_v}{k} \ln \frac{T_3}{T_2} = \ln \frac{V_L}{V_3} \quad \text{for} \quad 2 \rightarrow 3
\]

\[\Rightarrow \left( \frac{T_3}{T_2} \right)^{C_v/k} = \frac{V_L}{V_3}
\]

\[\left( \frac{T_3}{800} \right)^{C_v/k} = \frac{2}{1}
\]

\[\Rightarrow \text{Now} \quad \frac{C_v}{k} = \frac{5}{2} = \frac{5}{L}
\]

\[\Rightarrow T_3 = (2)^{45} \times 800 \quad \Rightarrow T_3 = 1056 K
\]

\[P_3 = \frac{nRT_3}{V_3} = 1 \times 8.314 \times 1056 \frac{1}{10^{-3}} = 8.78 \times 10^6 \quad \Rightarrow 86.6 \text{ atm}
\]

Summary:

1. \(P_1 = 66 \text{ atm} \quad T_1 = 800K \quad V_1 = 1L\)
2. \(P_2 = 33 \text{ atm} \quad T_2 = 800K \quad V_2 = 2L\)
3. \(P_3 = 86.6 \text{ atm} \quad T_3 = 1056K \quad V_3 = 1L\)
(c) \[ ds = \left( \frac{\partial s}{\partial T} \right)_{P} \, dT + \left( \frac{\partial s}{\partial P} \right)_{T} \, dP = n \left( \frac{\partial s}{\partial T} \right)_{P} \, dT - n \frac{\partial s}{\partial P} \, dP \]

\[ \text{Note:} \quad \left( \frac{\partial s}{\partial P} \right)_{T} = - \left( \frac{\partial V}{\partial T} \right)_{P} = \frac{n \kappa}{\rho} \, dP \]

1\rightarrow 2: \quad \Delta s_{1\rightarrow 2} = n R \ln \frac{P_2}{P_1} = n R \ln 2 = 5.76 \text{J/K} \]

2\rightarrow 3: \quad \Delta s_{2\rightarrow 3} = 0 \quad \text{Since the process is adiabatic} \]

3\rightarrow 1: \quad \Delta s_{3\rightarrow 1} = n R \ln 2 = 5.76 \text{J/K} \]

\[ \text{because the path is circular,} \quad \Delta s_{1\rightarrow 2} + \Delta s_{2\rightarrow 3} + \Delta s_{3\rightarrow 1} \text{ must be } 0 \]

(d) If the compression is irreversible but still adiabatic, more work would have to be put in.

\[ \Rightarrow \Delta U_{\text{irrev}} > \Delta U_{\text{rev}} \]

\[ \Rightarrow \text{ (for ideal gas)} \]

\[ T_{\text{irrev}} > T_{\text{rev}} \Rightarrow P_{\text{irrev}} > P_{\text{rev}} \]
\[ dF = -s \, dT - P \, dV \quad - (1) \]

\[ dF = \left( \frac{\partial F}{\partial P} \right)_T \, dP + \left( \frac{\partial F}{\partial T} \right)_P \, dT \quad - (2) \]

corresponding to (1) and (2)

\[ \left( \frac{\partial F}{\partial T} \right)_V = -s \quad \text{and} \quad \left( \frac{\partial F}{\partial V} \right)_T = -P \]

Next, \( \left( \frac{\partial F}{\partial P} \right)_T \) and \( \left( \frac{\partial F}{\partial T} \right)_P \)

\[ \left( \frac{\partial F}{\partial T} \right)_P = \left( \frac{\partial F}{\partial T} \right)_V + \left( \frac{\partial F}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P \]

\[ = -s + (-P)(V \Delta V) \]

\[ = -s - PV \Delta V \]

\[ \left( \frac{\partial F}{\partial P} \right)_T = \left( \frac{\partial F}{\partial V} \right)_T \left( \frac{\partial V}{\partial P} \right)_T \]

\[ = (-P)(-V \beta_T) = PV / \beta_T \]

\[ \Rightarrow dF = (-s - PV \Delta V) \, dT + (PV / \beta_T) \, dP \]
Question 4:

Do not draw more than one solution. Clearly specify your answer

Below is the Mn-Mo phase diagram.

a) The phase boundaries in the area that is circled (near 2220°C) are somewhat unclear. Please draw a possible (but thermodynamically correct) solution for the three-phase equilibria near 2220°C showing clearly how all single phase regions connect to the invariant three-phase equilibrium. If necessary, exaggerate, the width of single phase regions. Please do not draw on the phase diagram, but make a clear drawing below. You do not need to draw the complete phase diagram, only the relevant section involving Mo,G and L near 2220°C. Do not yet worry about the hashed rectangle, which is for part b of the question.
b) Your advisor spilled beer over part of the phase diagram, and as a result the region that is hashed on the previous page became illegible. On the diagram, below, please sketch a plausible solution for the missing region.

A possible solution
Note that every invariant (horizontal line) needs to involve a three-phase reaction.
Question 5:

$Y_2O_3-ZrO_2$ is a material of interest for sensors and solid oxide fuel cells. At the relevant temperature and composition range ZrO$_2$ forms a simple fluorite structure with an fcc array of Zr cations, and the oxygen ions occupying all the tetrahedral interstitials of this array.

As $Y_2O_3$ is added to ZrO$_2$, the Y cations substitute on the Zr sublattice. For charge compensation reasons, a vacancy needs to exist on the oxygen sublattice for each 2 Y cations added.

a) Assuming an ideal solution of Y and Zr on the cation sublattice, and oxygen and vacancies on the anion sublattice, write down the entropy of mixing as function of the mole fraction of Y cations on the cation sublattice.

b) In the real material, oxygen vacancies may be attracted to the Y cation, for electrostatic reasons or due to size effects. Describe how the entropy in part a) will change when such attractive interaction occurs.

\[ 2V \text{ sublattice} \rightarrow \text{Standard Bunch} \frac{(x_Y \ln x_Y + (1-x_Y) \ln (1-x_Y))}{(N_v/2)! (2N-N_v/2)!} \]

\[ \text{O sublattice} \rightarrow 2N \text{ sites}, \frac{N_v}{2} \text{ vacancies} \]

\[ \ln \frac{2N!}{(N_v/2)! (2N-N_v/2)!} = 2N \ln \frac{2N}{2N-2N} - \frac{N_v}{2} \ln \frac{N_v}{2} + \frac{N_v}{2} - (2N-\frac{N_v}{2}) \ln (2N-\frac{N_v}{2}) + 2N - \frac{N_v}{2} \]

\[ = \frac{N_v}{2} \ln \frac{4N}{N_v} + (2N-\frac{N_v}{2}) \ln \frac{2N}{2N-\frac{N_v}{2}} \]

\[ = \frac{N_v}{2} \ln \frac{1}{N_v} + (2N-\frac{N_v}{2}) \ln \frac{1}{1-\frac{N_v}{4N}} \]

\[ = - \left[ \frac{N_v}{2} \ln \frac{x_Y}{x_Y} + (2N-\frac{N_v}{2}) \ln 1 - \frac{x_Y}{x_Y} \right] \]

\[ \text{divide by } 2N \]

\[ - \left[ \frac{x_Y}{x_Y} \ln \frac{1}{1} + (1-\frac{x_Y}{x_Y}) \ln 1 - \frac{x_Y}{x_Y} \right] \]

b. goes down
QUESTION 6

- At constant T, P, the heat that evolves during a change of state is equal to the change of the enthalpy between the final & initial state.

- The final state is a solid solution on the fcc lattice. But pure A at 1200 K is a liquid.

- Therefore, first need enthalpy difference between the solid & liquid state of pure A at 1200 K

\[ \Delta H^{\text{f-s}} = \] for pure A

\[ \Rightarrow \frac{\Delta H^{\text{f-s}}}{\text{mol}} = -4.1 \text{ kJ/mol} \]

8 mol of A \( \Rightarrow \Delta H^{\text{f-s}} = -12 \text{ kJ} \)

- Enthalpy change upon mixing solid A & solid B

\[ \Delta H_{\text{mix}} = x_A x_B \times (-12000) = (0.3)(0.7)(-12000) = -2646 \text{ J/mol} \]

A total of 10 moles

\[ \Rightarrow \Delta H_{\text{mix}} = 10(-2646) = -26460 \text{ J} = -26.460 \text{ kJ} \]

\[ Q = \Delta H_{\text{total}} = \Delta H^{\text{f-s}} - 12 \text{ kJ} - 26.460 \text{ kJ} \]

\[ = -38.46 \text{kJ} \]

or -38.46 kJ of heat is released upon mixing.
Question 7 (Short questions):

a) Define the Legendre transform of the entropy that gives a function with natural variables $1/T$ and $p/T$.

b) A material (closed system) at constant pressure undergoes a reversible phase transition with temperature at $T = T_0$. Please indicate whether the following statements are always true, true only part of the time, or never true.

At the phase transition temperature the high temperature phase has a higher volume than the low-temperature phase:

- NEVER TRUE  - ALWAYS TRUE  - TRUE PART OF THE TIME

At the phase transition temperature $T_0$, the high temperature phase has a higher entropy than the low-temperature phase:

- NEVER TRUE  - ALWAYS TRUE  - TRUE PART OF THE TIME

At the phase transition temperature $T_0$ the high temperature phase has a higher enthalpy than the low-temperature phase:

- NEVER TRUE  - ALWAYS TRUE  - TRUE PART OF THE TIME

At the phase transition temperature $T_0$ the high temperature phase has a higher Gibbs free energy than the low-temperature phase:

- NEVER TRUE  - ALWAYS TRUE  - TRUE PART OF THE TIME

c) A metal always has a higher electronic entropy than an oxide

- TRUE  - FALSE
d) For a system with only pdV work, in an environment under constant pressure and temperature, the condition that $\Delta S_{\text{universe}} > 0$ is equivalent to:

\[
\begin{align*}
\Delta G > 0 & \quad \times \quad \Delta G < 0 & \quad \Delta H < 0 & \quad \Delta H > 0 & \quad \Delta S < 0 \\
\times & \quad \Delta S > 0
\end{align*}
\]

In the above, the state functions (G,H,S) refer to properties of the system.

e) At constant composition, does the free energy increase or decrease with increasing temperature?

\[
\begin{align*}
\text{INCREASE} & \quad \times \quad \text{DECREASE}
\end{align*}
\]
a) Energy spectrum of a harmonic oscillator

\[ E_n = (n + \frac{1}{2}) \hbar \omega \]

\[ q_A^x = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega (n + \frac{1}{2})} = \frac{e^{-\beta \hbar \omega \frac{1}{2}}}{1 - e^{-\beta \hbar \omega}} \quad \text{with} \quad \nu = \frac{\nu_A}{2} \]

geometric series

b) Free energy for \( x \)-phase (pure A, all atoms are non-interacting) and localised on a lattice

\[ q_A^x = \left( \frac{q_A}{N_A} \right)^{N_A^x} \]

\[ N_A^x = \text{total number of A atoms in } x \]

\[ F_x = -kT \ln q_A^x \]

\[ = -N_A^x kT \ln \left( \frac{q_A}{N_A} \right)^{N_A^x} \]

Free energy for \( \beta \)-phase

\[ q_\beta = \frac{N_B^\beta!}{(N_A^\beta)! (N_B^\beta)!} \left( \frac{q_A^x}{N_A^x} \right)^{N_A^\beta} \left( \frac{q_B^y}{N_B^y} \right)^{N_B^\beta} \]

\[ N_A^\beta = \text{total number of atoms in } \beta \]

\[ N_A^\beta = \# \text{ of A atoms in } \beta \]

\[ N_B^\beta = \# \text{ of B atoms in } \beta \]

Arises due to configurational degrees of freedom

\[ G_\beta = -kT \ln q_\beta \]

\[ = -N_A^\beta kT \ln q_A^\beta - N_B^\beta kT \ln q_B^\beta + N_b^\beta kT \left\{ x_A \ln x_A + x_B \ln x_B \right\} \]

\[ x_A = \frac{N_A^\beta}{N_A^\beta} \quad \frac{x_A}{N_B^\beta} \]
c) Solubility at limit of $A$ in $B$

Comes from 2-phase equilibrium between $\alpha$ and $\beta$

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure $A$</td>
<td>mixture of $A$ and $B$</td>
</tr>
</tbody>
</table>

Equilibrium:

$\text{N}^d_A = \text{N}^a_A$

$\text{N}^d_A = \frac{2F^d}{2N^d} = -kT \ln q^d_A$

$\text{N}^a_A = \frac{2F^a}{2N^a} = -kT \ln q^a_A + kT \ln x^a_A$

(x Solubility)

$\text{N}^d_A + kT \ln x^a_A$

$x^a_A$ solubility: $\left( \frac{q^a_A}{q^d_A} \right)$