Please do your own work, relax and take your time.
Remember, this is only a test.

The following information may be useful:

\[
1 \text{ m}^3 = 1000 \text{ L} = 1000 \text{ dm}^3 \quad \quad 1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}
\]

\[
\int \frac{dx}{x} = \ln x \quad \quad \int dx = x \quad \quad N! = \left( \frac{N}{e} \right)^N
\]

1. Determine the entropy of mixing three different substances.
   a) (10 pts) Start with three separate lattices with A, B and D sites and a, b, and d
   particles, respectively. Find an expression for the change in entropy on going from the
   three separate systems to one combined system where the particles are still
distinguishable. In other words, find \( \Delta S = S_{\text{combined}} - S_{\text{separate}} \). Do not employ any
   approximations and perform only obvious simplification (leave things as factorials and
   don’t work hard to make it look nice).

\[
W_A = \frac{A!}{a! (A-a)!} \quad \quad W_B = \frac{B!}{b! (B-b)!} \quad \quad W_0 = \frac{D!}{d! (D-d)!}
\]

\[
W_{\text{SEPARATE}} = W_A W_B W_0 = \frac{A! B! D!}{a! (A-a)! b! (B-b)! d! (D-d)!}
\]

\[
W_{\text{COMBINED}} = \frac{(A+B+D)!}{a! b! d! (A+B+D-a-b-d)!}
\]

\[
\Delta S = k \ln \frac{W_{\text{COMBINED}}}{W_{\text{SEPARATE}}} = k \ln \frac{W_{\text{COMBINED}}}{W_{\text{SEPARATE}}}
\]

\[
\Delta S = k \ln \left[ \frac{(A+B+D)!}{a! (A-a)! b! (B-b)! d! (D-d)!} \right] \frac{a! (A-a)! b! (B-b)! d! (D-d)!}{a! b! d! (A+B+D-a-b-d)! A! B! D!}
\]

\[
\Delta S = k \ln \left[ \frac{(A+B+D)! (A-a)! (B-b)! (D-d)!}{A! B! D! (A+B+D-a-b-d)!} \right]
\]
b) (6 pts) Now assume that all of the lattices are the same size and that there are the same number of each type of particle, i.e. \( A = B = D \) and \( a \equiv b = d \). Simplify your expression from part a) as much as possible, assuming that \( A \) and \( a \) are both very large.

\[
\Delta S = k \ln \left[ \frac{(3A)! (A-a)!)^3}{(A!)^3 (3A-3a)!} \right]
\]

Use Stirling's Approx

\[
\Delta S = k \ln \left[ \frac{(3A/e)^3 (A-a) \cdot \left( \frac{e}{A-a} \right)^{A-a}}{(A/e)^3 (3A-3a) \cdot \left( \frac{e}{3A-3a} \right)^{3A-3a}} \right]
\]

\[
\Delta S = k \ln \left[ \frac{(3A)^3 (A-a) \cdot \left( \frac{e}{A-a} \right)^{A-a}}{A^3 (3A-3a) \cdot \left( \frac{e}{3A-3a} \right)^{3A-3a}} \right] \left( \frac{e^{-3A}}{e^{-3A+3a}} \right)^{1}
\]

\[
\Delta S = k \left[ 3A \ln(3A) + (3A-3a) \ln(A-a) - 3A \ln A - (3A-3a) \ln(3A-3a) \right]
\]

\[
\Delta S = k \left[ 3A \ln 3 + 3A \ln A - 3A \ln A + (3A-a) \ln(A-a) - (3A-a) \ln(A-a) - (3A-3a) \ln 3 \right]
\]

\[
\Delta S = k \left[ 3A \ln 3 - 3A \ln 3 + 3a \ln 3 \right]
\]

\[
\Delta S = 3a \cdot k_B \ln 3
\]

\[
\Delta S = k_B \ln 3^a = k_B \ln 27^a
\]

2. (4 pts) Compare the intermolecular interactions between HF molecules to that between H₂ molecules. Which one statement is false?

a) HF molecules participate in dispersion interactions
b) H₂ molecules participate in dispersion interactions
c) HF has a higher boiling point than H₂
d) The Van der Waals equation "a" coefficient for H₂ is greater
3. (10 pts) $\text{CO}_2$ remains solid up to $-78 ^\circ\text{C}$ and $\text{CO}$ remains solid only to $-205 ^\circ\text{C}$. Explain how this can be true when $\text{CO}$ has a dipole moment of 0.11 Debye and $\text{CO}_2$ has a dipole moment of zero. (Hint, there are at least two good reasons.)

\[
\text{C} \equiv \text{O} \quad \text{O} \equiv \text{C} \equiv \text{O}
\]

Even though $\text{CO}_2$ has no dipole moment, it does have slightly negative oxygen and a positive carbon. So, when $\text{CO}_2$'s are close together they are attracted strongly by electrostatics — stronger than $\text{CO}$ since it has two dipoles rather than one.

Because $\text{CO}_2$ also has more total electrons than $\text{CO}$, the dispersive attraction is stronger between $\text{CO}_2$ than $\text{CO}$.

4. a) (4 pts) Let’s define a new function called the Dill energy, $D = G - \mu N$. Given that the fundamental thermodynamic equation for the Gibbs free energy is $dG = -SdT + Vdp + \mu dN$, derive the fundamental thermodynamic equation for the Dill energy.

\[
\begin{align*}
D &= G - \mu N \\
\frac{dD}{dN} &= \frac{dG}{dN} - \mu - ND \mu \\
\frac{dD}{dV} &= -SdT + Vdp + \mu dN - ND\mu \\
\frac{dD}{dT} &= -S + Vdp - ND\mu
\end{align*}
\]

b) (3 pts) What are the natural variables of the Dill energy?

$T, p, \mu$
c) (8 pts) Derive any one of the Maxwell relations associated with the Dill energy. (Justify your steps carefully.)

\[ dD = -SdT + VdP \]

Since \( G, \mu, +N \) are all state functions, \( dD \) must also be a state function.

Since \( D \) is a state function, \( dD \) must be exact.

\[ \frac{d}{dp}(-S)_T = \frac{\partial}{\partial T}(V)_P \]

\[ -(\frac{\partial S}{\partial P})_T = (\frac{\partial V}{\partial T})_P \]

5. Assume that we have one mole of ideal gas at 10 atm and 300 K. This is point I. The heat capacity of the gas is \( C_p = \frac{5}{2}R \).

a) (18 pts) The gas expands reversibly and adiabatically to a final pressure of 1 atm. This is point II. Calculate the values of \( \Delta S, \Delta U, \Delta H, q \), and \( w \) for this expansion from I to II. (You also have space on the next page for this)

**Adiabatic** \( \Rightarrow \quad q = 0 \)

\[ \Delta S = \left( 5\frac{q}{T} \right)_T = 0 \]

**We'll need** \( T_{final} \) **to find the rest**

\[ P_i V_i^\gamma = P_f V_f^\gamma \]

\[ 10 \text{ atm} \quad V_i^{\gamma/5} = 1 \text{ atm} \quad V_f^{\gamma/5} \]

\[ V_i = \frac{nRT_i}{P_i} = \frac{(1)(0.08206)(300K)}{10} = 2462 \text{ L} \]

\[ 10 \text{ atm} \quad \text{Lam} = \left( \frac{V_f}{2462 \text{ L}} \right)^{7/5} \]

\[ V_f = (10^{5/7}) \times 2462 \text{ L} = 12.75 \text{ L} \]
5 a) continued

\[
\left( \frac{T_\Pi}{T_\Pi} \right)^{C_v/\kappa} = \frac{V_\Pi}{V_\Pi} \quad \left( \frac{T_\Pi}{300} \right)^{5/2} = \frac{2,462}{12,75}
\]

\[\frac{T_\Pi}{12,75} = \left( \frac{2,462}{12,75} \right)^{3/5} 300 K = 155,38 K \]

\[
\Delta U = \int_{T_\Pi}^{155,4} C_v dT
\]

\[= \int_{300}^{\frac{5}{2}(8,3145)} dT
\]

\[= \frac{5}{2}(8,3145)(155,4 - 300)
\]

\[\Delta U = -3,0 kJ
\]

\[\omega = \Delta U = -3,0 kJ
\] \text{ (expansion w<0)}

\[
\Delta H = \int_{T_\Pi}^{155,4} C_p dT
\]

\[\Delta H = \frac{7}{2}(8,3145)(155,4 - 300)
\]

\[\Delta H = -4,2 kJ
\]

FROM EARLIER

\[q = 0
\]

\[\Delta S = 0
\]
b) (12 pts) Assume we are back at point I and this time let the gas expand reversibly and isothermally to a final pressure of 1 atm. This is point III. Calculate the values of $\Delta S$, $\Delta U$, $\Delta H$, $q$, and $w$ for this expansion from I to III.

$$V_{III} = \frac{nRT_{III}}{P_{III}} = \frac{(1)(0.08206 \times 300 \text{ K})}{1} = 24.618 \text{ L}$$

\text{ISOHERMAL} \Rightarrow \begin{align*}
\Delta U &= 0 \\
\Delta H &= 0
\end{align*}

$$w = -\int p \, dV = -nRT \frac{dV}{V} = -(1)(8.3145 \times 300 \text{ K}) \ln \left( \frac{24.618}{2.4618} \right)$$

$$w = -5.74 \text{ kJ}$$

$$q = -w = 5.74 \text{ kJ}$$

$$\Delta S = \int \frac{q}{T} = \int \frac{nw}{V} \, dV = (1)(8.3145) \ln \left( \frac{24.618}{2.4618} \right)$$

$$\Delta S = 19.1 \text{ J/K}$$

c) (8 pts) Illustrate the amounts of work calculated in parts a) and b) on a single $P-V$ plot. Label the axes and any key points.
d) (10 pts) Now assume that we are conducting a cycle from point I to point II, then from II to III, and finally from III back to I. Calculate the values of \( \Delta S \), \( \Delta U \), \( \Delta H \), \( q \), and \( w \) for the isobaric process that takes us from point II to point III.

\[
\omega_{II-III} = -\int_{VII}^{VIII} \rho dV = -\rho (V_{VIII} - V_{VII}) = - (11,87 \text{ L atm}) (24.62 - 12.75 \text{ L}) = -11.87 \text{ kJ}
\]

(Note: \( w < 0 \))

\[
\Delta U = \int_{VII}^{VIII} \frac{C_v}{T} dT = \frac{5}{2} (8.3145)(300K - 155.38K)
\]

\[\Delta U = 3,10 \text{ kJ}\]

\[
\Delta H = \int_{VII}^{VIII} C_p dT = \frac{7}{2} (8.3145)(300K - 155.38K)
\]

\[\Delta H = 4,2 \text{ kJ}\]

\[q = \Delta U - w = \Delta H = 4,2 \text{ kJ}\]

\[\Delta S = \int_{VII}^{VIII} \frac{q}{T} dT = \int \frac{C_p}{T} dT = C_p \ln \left( \frac{T_{VIII}}{T_{VII}} \right) = \frac{7}{2} (8.3145) \ln \left( \frac{300K}{155.38K} \right)
\]

\[\Delta S = 19.14 \text{ J/K}\]

e) (7 pts) Finally, calculate the values of \( \Delta S \), \( \Delta U \), \( \Delta H \), \( q \), and \( w \) for the entire cycle from I to II to III to I.

Note: Last step (III - I), so opposite of Part b)

\[\omega = -3,0 \text{ kJ} + 5,74 \text{ kJ} - 1,2 \text{ kJ} = 1,54 \text{ kJ} = \Delta U\]

\[q = 0 - 5,74 \text{ kJ} + 4,2 \text{ kJ} = -1,54 \text{ kJ} = \Delta H\]

\[\Delta U = -3,0 \text{ kJ} - 0 + 3,0 \text{ kJ} = 0 = q\]

\[\Delta H = -4,2 \text{ kJ} - 0 + 4,2 \text{ kJ} = 0 = \Delta S\]

\[\Delta S = 0 - 19.1 \text{ J/K} + 19.1 \text{ J/K} = 0\]