1. (20 points) True or False?
   a. A Carnot cycle is by definition a reversible cycle. (TRUE) (FALSE)
   b. If a system absorbs heat, its entropy must increase. (TRUE) (FALSE)
   c. The entropy (S) of 20 g of H₂O(l) at 300 K and 1 bar is twice the entropy of 10 g of H₂O(l) at 300 K and 1 bar. (TRUE) (FALSE)
   d. ΔS for 1 mol of N₂(g) going irreversibly from 25 °C and 10 L to 50 °C and 20 L must be the same as ΔS for 1 mol of N₂(g) going reversibly from 25 °C and 10 L to 50 °C and 20 L. (TRUE) (FALSE)
   e. For a closed system, ΔS can never be negative. (TRUE) (FALSE)
   f. The quantities of SdT, TdS, VdP, and PdV all have the dimensions of energy. (TRUE) (FALSE)
   g. The Gibbs energy of 12 g of ice at 0 °C and 1 bar is less than the Gibbs energy of 12 g of liquid water at 0 °C and 1 bar. (TRUE) (FALSE)
   h. The chemical potential, μ, is a state function. (TRUE) (FALSE)
   i. The chemical potential of benzene in a solution of benzene and toluene must equal to the chemical potential of toluene in that solution. (TRUE) (FALSE)
   j. ΔG = 0 and ΔS = 0 for a reversible phase transition at constant T and P. (TRUE) (FALSE)

2. (20 pts) Consider a Carnot heat engine that uses reservoirs at 800 °C and 0 °C. (a) Calculate the efficiency of the engine? (b) If 1300 J is released at 0 °C, how much heat is absorbed at 800 °C? What is the maximum possible work done by this heat engine?

(a) The efficiency of a Carnot heat engine is (equation 5.4 and 5.9)
\[ \varepsilon = 1 - \frac{T_c}{T_H} = 1 - \frac{273.15}{273.15 + 800} = 0.7456 \]

(b) \[ \varepsilon = -\frac{w}{q_H} = 0.7456 \ldots\ldots(1) \]
\[ q_H = q_C - w \ldots\ldots(2) \]
\[ q_C = 1300 \text{ (J)} \ldots\ldots(3) \]
Solving equation (1), (2) and (3): \[ q_H = 5110.06 \text{ (J)} \]
\[ w = -3810.06 \text{ (J)} \]
3. (20 pts) Using equations (6.17 – 6.20) on page 130, derive the four Maxwell relations (listed below). Note that jumping directly from equations (6.22 – 6.25) to equations (6.26 – 6.29) is not acceptable. You need to show detailed steps of derivation.

(a) \( U \) is a state function, \( \therefore \)
\[
\left[ \frac{\partial}{\partial T} \left( \frac{\partial U}{\partial S} \right)_V \right]_S = \left[ \frac{\partial}{\partial S} \left( \frac{\partial U}{\partial V} \right)_T \right]_V \quad (1)
\]
\[\vdots\]
\[dU = TdS - PdV\]
\[
\left[ \frac{\partial U}{\partial S} \right]_V = T; \left[ \frac{\partial U}{\partial V} \right]_S = -P, \text{ substitute into eqn. (1):}
\]
\[\Rightarrow \left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V \text{ Q.E.D.}
\]

(b) \( H \) is a state function,
\[
\left[ \frac{\partial}{\partial P} \left( \frac{\partial H}{\partial S} \right)_T \right]_S = \left[ \frac{\partial}{\partial S} \left( \frac{\partial H}{\partial P} \right)_T \right]_P \quad (2)
\]
\[\vdots\]
\[dH = TdS + VdP\]
\[
\left[ \frac{\partial H}{\partial S} \right]_P = T; \left[ \frac{\partial H}{\partial P} \right]_S = V, \text{ substitute into eqn. (2):}
\]
\[\Rightarrow \left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P \text{ Q.E.D.}
\]

(c) \( A \) is a state function,
\[
\left[ \frac{\partial}{\partial S} \left( \frac{\partial A}{\partial V} \right)_T \right]_T = \left[ \frac{\partial}{\partial T} \left( \frac{\partial A}{\partial V} \right) \right]_V \quad (3)
\]
\[\vdots\]
\[dA = -SdT - PdV\]
\[
\left( \frac{\partial A}{\partial T} \right)_V = -S; \left( \frac{\partial A}{\partial V} \right)_T = -P, \text{ substitute into eqn. (3):}
\]
\[\Rightarrow \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \text{ Q.E.D.}
\]

(d) \( G \) is a state function,
\[
\left[ \frac{\partial}{\partial P} \left( \frac{\partial G}{\partial T} \right)_V \right]_T = \left[ \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial P} \right)_V \right]_P \quad (4)
\]
\[\vdots\]
\[dG = -SdT + VdP\]
\[
\left( \frac{\partial G}{\partial T} \right)_P = -S; \left( \frac{\partial G}{\partial P} \right)_T = V, \text{ substitute into eqn. (4):}
\]
\[\Rightarrow - \left( \frac{\partial S}{\partial P} \right)_T = \left( \frac{\partial V}{\partial T} \right)_P \text{ Q.E.D.}
\]
4. (20 pts) An ideal gas has $C_{v,m} = a + bT$ with $a = 25.0 \text{ J/(mol K)}$ and $b = 0.03 \text{ J/(mol K}^2)$. If 4 mol of this gas go from 300 K and 2 bars to 500 K and 3 bar, calculate each of the following quantities for this change of state: (a) $q$, (b) $w$, (c) $\Delta U$, (d) $\Delta H$, and (e) $\Delta S$. If it is impossible to calculate a quantity from the given information, state this.

Since ideal gas and $C_{v,m}$ depends on temperature, the work $w$ and heat $q$ are impossible to calculate because they are path functions and no information about the path is given in this question.

$$\Delta U = \int_{T_1}^{T_2} nC_{v,m} \, dT = \int_{T_1}^{T_2} n(a + bT) \, dT = na(T_2 - T_1) + \frac{n}{2} b(T_2^2 - T_1^2)$$

$$= 4 \times 25 \times (500 - 300) + 2 \times 0.03 \times (500^2 - 300^2) = 29600 \text{ (J)}$$

$$\Delta H = \int_{T_1}^{T_2} nC_{p,m} \, dT = \int_{T_1}^{T_2} n(C_{v,m} + R) \, dT = \Delta U + nR(T_2 - T_1)$$

$$= 29600 + 4 \times 8.314 \times (500 - 300) = 36251.2 \text{ (J)}$$

$$\Delta S = \int_{T_1}^{T_2} nC_{p,m} \, dT - \int_{P_1}^{P_2} \frac{nR}{T} \, dP = n \int_{T_1}^{T_2} \frac{(a + bT + R) \, dT}{T} - nR \ln \frac{P_2}{P_1}$$

$$= n[(a + R) \ln \frac{T_2}{T_1} + b(T_2 - T_1) - R \ln \frac{P_2}{P_1}]$$

$$= 4 \times [(25 + 8.314) \times \ln \frac{500}{300} + 0.03 \times (500 - 300) - 8.314 \times \ln \frac{3}{2}] = 78.49 \text{ (J/K)}$$
5. (20 pts) For the reaction \( \text{N}_2\text{O}_4(g) \rightarrow 2\text{NO}_2(g) \) in the temperature range of 298 K to 900 K, equilibrium constant \( K_p = aT^be^{-c/T} \), where \( a = 1.09 \times 10^{13} \), \( b = -1.304 \), and \( c = 7307 \). Note that the term “T” is the value of the temperature but without the unit. (a) Find the mathematical expressions for \( \Delta G^\circ \), \( \Delta H^\circ \), and \( \Delta S^\circ \) as a function of \( T \). (b) Calculate \( \Delta H^\circ \) at 300 and 600 K.

(a) \( \Delta G^\circ = -RT \ln K_p = -RT \ln(aT^b e^{-c/T}) = -RT \ln a - bRT \ln T + cR \) (equation 6.61)

Starting here, there are two ways to derive \( \Delta H^\circ \) and \( \Delta S^\circ \):

=====Way #1=====

\[ \therefore dG = -SdT + VdP \]

\[ \therefore \left( \frac{\partial G}{\partial T} \right)_p = -S \Rightarrow \left( \frac{\partial \Delta G^\circ}{\partial T} \right)_{p=p^o} = -\Delta S^\circ \]

\[ \therefore \Delta S^\circ = \left( \frac{\partial \Delta G^\circ}{\partial T} \right)_{p=p^o} = R \ln a + bR \ln T + bR \]

\[ \therefore \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]

\[ \therefore \Delta H^\circ = \Delta G^\circ + T \Delta S^\circ = -RT \ln a - bRT \ln T + cR + RT \ln a + bRT \ln T + bRT \]

\[ = bRT + cR = R(c + bT) \]

=====Way #2=====

Use Gibbs-Helmholtz equation

\[ \left[ \frac{\partial \left( \frac{\Delta G^\circ}{T} \right)}{\partial T} \right]_p = \frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2} \] (equation 6.64)

\[ \Rightarrow \Delta H^\circ = RT^2 \times \frac{d \ln K_p}{dT} = RT^2 \times \frac{d}{dT} \left( \ln a + b \ln T - \frac{c}{T} \right) = RT^2 \left( \frac{b}{T} + \frac{c}{T^2} \right) \]

\[ = R(c + bT) \]

\[ \therefore \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \] (equation 6.14)

\[ \therefore \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{cR + bRT + RT \ln a + bRT \ln T - cR}{T} \]

\[ = R \ln a + bRT \ln T + bR \]

(b)

\[ \therefore \Delta H^\circ = R(c + bT) \]

\[ \therefore \Delta H^\circ (T = 300 \text{ K}) = 8.314 \times (7307 - 1.304 \times 300) = 57498 \text{ (J/mol or J)} \]

\[ \Delta H^\circ (T = 600 \text{ K}) = 8.314 \times (7307 - 1.304 \times 600) = 54246 \text{ (J/mol or J)} \]