Calorimetric calculations:

\[ dQ = mc \, dT \quad \text{or} \quad dQ = nC_v \, dT \quad \text{(specific heat)} \]
\[ Q = mL \quad \text{(latent heat)} \]

General Formulas applicable to ALL processes in an Ideal Gas:

\[ PV = nRT \]
\[ dU = dQ - dW \]
\[ dW = PdV \]
\[ dU = nC_v \, dT \]

Specific Processes:

**Isothermal:** \( T=\text{constant} \rightarrow dT = 0 \rightarrow dU = 0 \rightarrow dQ = dW \)
\[ W = \int PdV = \int nRT \frac{dV}{V} = nRT \ln \left( \frac{V_f}{V_i} \right) \]

**Adiabatic:** \( dQ = 0 \rightarrow dU = -dW \)
\[ dW = -dU \rightarrow W = -\int nC_v \, dT = nC_v \left( T_f - T_i \right) \]
\[ PV^{\gamma} = \text{const} \]
\[ TV^{\gamma - 1} = \text{const} \]

**Isobaric:** \( P=\text{constant} \)
\[ \rightarrow W = \int PdV = P \left( V_f - V_i \right) \]

**Isochroic:** \( V=\text{constant} \rightarrow dV = 0 \rightarrow dW = 0 \rightarrow dU = dQ \)
Entropy:

**General Reversible Processes:** \( dS = \frac{dQ}{T} \)

\[ \Rightarrow \Delta S = nC_v \ln \left( \frac{T_f}{T_i} \right) + nR \ln \left( \frac{V_f}{V_i} \right) \]

**Calorimetric Processes:**

*(specific heat)*: \( dQ = mc \frac{dT}{T} \) or \( dQ = nCdT \)

\[ \Rightarrow dS = mc \frac{dT}{T} \quad \text{or} \quad = nC \frac{dT}{T} \]

\[ \Rightarrow \Delta S = mc \ln \left( \frac{T_f}{T_i} \right) \quad \text{or} \quad = nC \ln \left( \frac{T_f}{T_i} \right) \]

*(latent heat)*: \( Q = mL \)

\[ \Rightarrow \Delta S = \frac{mL}{T} \quad \text{[} T \text{ remains constant at phase change] } \]

**Non Reversible Processes:** (one cannot write \( dS = \frac{dQ}{T} \) for the process)

But one can use a surrogate reversible process with the same initial and final states to calculate \( \Delta S \).

**2nd Law of Thermodynamics:**

\[ \Delta S_{\text{tot}} = \Delta S_{\text{system}} + \Delta S_{\text{environment}} \geq 0 \]
1. **(25 pts)** Answer the following questions. (Use the space provided below and on the next page if needed.)

a). **(9 pts)** An ideal gas is reversibly expanded from an initial state \( i \) to the final state \( f \) through three different thermodynamic processes (a, b, c).

i) Which process will result in the largest \( \Delta U \)?

ii) Which process will result in the largest work done by the gas \( W \)?

iii) Which process will absorb the largest amount of heat \( Q \)?

b). **(8 pts)** A Carnot engine operates between a high temperature reservoir at \( T_H \) and a low temperature reservoir at \( T_L \). One can increase the efficiency of the engine by either increasing \( T_H \) by \( \Delta T \) or decreasing \( T_L \) by \( \Delta T \). Which change \((T_H + \Delta T)\) or \((T_L - \Delta T)\) will result in a larger efficiency for the engine?

c). **(8 pts)** i) An ideal gas is being taken from an initial temperature \( T_i \) to a final temperature \( T_f \) in two separate processes: (a) isobaric and (b) isochoric, as shown.

i) Will the entropy of the system decrease or increase in both processes?

ii) Which process will result in a larger change in the system’s entropy?

SOLUTION:

a) i) \( U \) is a state variable. Since all three processes (a, b, & c) have the same initial and final states, we have \( \Delta U_a = \Delta U_b = \Delta U_c \).

ii) Work done by the gas is the area under the curve. From the graph shown, we have the following ranking \( W_a > W_b > W_c \).
iii) From the 1st Law, we have $Q = \Delta U + W$. Since all $\Delta U$’s are the same, the ranking for $Q$ will be the same as the ranking for $W$, i.e., $Q_a > Q_b > Q_c$.

b) For a Carnot engine, the efficiency is given by $e = 1 - \frac{T_L}{T_H}$ so that both decreasing $T_L$ and/or increasing $T_H$ will give a smaller $\frac{T_L}{T_H}$ and makes $e$ closer to 1. As for a fixed change in temperature, $\Delta T$, the ratio $\frac{T_L - \Delta T}{T_H}$ will generally be smaller than $\frac{T_L}{T_H} + \Delta T$ so that $e(T_L \to T_L - \Delta T) > e(T_H \to T_H + \Delta T)$.

To see that, we can consider the following ratio:

$$\frac{(T_L - \Delta T)/T_H}{T_L/(T_H + \Delta T)} = \frac{T_L T_H - (T_H - T_L) \Delta T - \Delta T^2}{T_L T_H} = 1 - \frac{T_H - T_L}{T_L T_H} \Delta T - \frac{1}{T_L T_H} \Delta T^2 < 1$$

Both blue terms are positive so that this ratio will always be less than 1 indicating that,$$
\frac{T_L - \Delta T}{T_H} \text{ will always be smaller than } \frac{T_L}{T_H + \Delta T}.
$$

c) i) In both processes (isobaric and isochoric), heat enters the system as the temperature increases. Since $dS = dQ/T$, the change in entropy for both processes will also be positive (an increase).

iii) For this problem, the change in temperature for both processes is the same. Since $C_p > C_v$, we have $dQ_p > dQ_v$ and $\Delta S_p > \Delta S_v$.

$$\text{note: } \Delta S_{p,v} = \int_{T_i}^{T_f} \frac{dQ_{p,v}}{T} = nC_{p,v} \int_{T_i}^{T_f} \frac{dT}{T} = nC_{p,v} \ln \left( \frac{T_f}{T_i} \right)$$

Thus, the isobaric process will result in a larger entropy increase.
2. (25 pts)
In a calorimetry experiment, a piece of hot iron initially at 500°C was placed in 1.50g of water at 20.0°C. After the system has come to equilibrium, all water was vaporized and the final temperature for the steam and hot iron was measured to be at 110°C? What was the mass of the hot iron?

\[
L_v = 22.6 \times 10^2 \frac{J}{g \cdot ^oC} \quad c_{steam} = 2.080 \frac{J}{g \cdot ^oC} \quad c_{water} = 4.186 \frac{J}{g \cdot ^oC} \quad c_{iron} = 0.450 \frac{J}{g \cdot ^oC}
\]

Let the mass of the iron piece be \( m_i \)

\[\sum Q = 0 \quad \text{gives} \]

\[
\left(\text{heat released, hot iron cooling } 500^\circ C \rightarrow 110^\circ C\right) + \left(\text{heat absorbed, water warming } 20^\circ C \rightarrow 100^\circ C\right) + \left(\text{latent heat absorbed to vaporize at } 100^\circ C\right) + \left(\text{heat absorbed, steam warming } 100^\circ C \rightarrow 110^\circ C\right) = 0
\]

This gives

\[m_i c_i (110^\circ C - 500^\circ C) + m_w c_w (100^\circ C - 20^\circ C) + m_L v + m_w c_s (110^\circ C - 100^\circ C) = 0\]

Rearranging terms, we then can solve for \( m_i \),

\[m_i = \frac{m_w [c_w (80^\circ C) + L_v + c_s (10^\circ C)]}{c_i (390^\circ C)}\]

\[m_i = \frac{(1.50g) \left[ (4.186 \frac{J}{g \cdot ^oC})(80.0^oC) + (22.6 \times 10^2 \frac{J}{g \cdot ^oC}) + (2.08 J/g \cdot ^oC)(10.0^oC) \right]}{(0.450 \frac{J}{g \cdot ^oC})(390^\circ C)}\]

\[m_i = \frac{(1.50g) \left[ (4.186 \frac{J}{g \cdot ^oC})(80.0^oC) + (22.6 \times 10^2 \frac{J}{g \cdot ^oC}) + (2.08 J/g \cdot ^oC)(10.0^oC) \right]}{(0.450 \frac{J}{g \cdot ^oC})(390^\circ C)}\]

\[m_i = 22.4 g\]

22.4g of hot iron was initially used in the calorimetry experiment.
3. (25 pts) 
A Carnot cycle operated between two temperature reservoirs at \(T_H=500^\circ\text{C}\) and \(T_L=200^\circ\text{C}\) has one mole of an ideal monoatomic gas as its working substance. You are given the following parameters for the cycle: \(V_A=10.0\text{L}, \ V_B=20.0\text{L}\). Calculate a) the net work done by the gas per cycle, b) the heat absorbed by the gas per cycle, c) the heat expelled by the gas per cycle. d) What is the efficiency of this cycle? 

\([1L = 10^{-3} \text{m}^3, 1\ \text{atm} = 1.013 \times 10^5 \text{Pa}]\)

To get the volume at state C and D, we can use the adiabatic processes:

\[ T_c V_c^{\gamma-1} = T_b V_b^{\gamma-1} \]

\[ V_c = V_B \left( \frac{T_H}{T_L} \right)^{(\gamma-1)/\gamma} = 20L \left( \frac{500 + 273.15}{200 + 273.15} \right)^{3/2} = 41.776L \]

Similarly,

\[ T_D V_D^{\gamma-1} = T_A V_A^{\gamma-1} \]

\[ V_D = V_A \left( \frac{T_H}{T_L} \right)^{(\gamma-1)/\gamma} = 10L \left( \frac{500 + 273.15}{200 + 273.15} \right)^{3/2} = 20.888L \]

Note that since we really only need the ratio \(V_D/V_C\), we can simply divide the above two equations (without doing the numerical calculations) to get

\[ \frac{V_D}{V_C} = \frac{V_A}{V_B} = 0.5. \]

a) Net work done by the cycle:

Isothermal branches (A→B, C→D) (\(\Delta U = 0\)):

\[ W_{AB} = nRT_H \ln \left( \frac{V_B}{V_A} \right) \quad \text{(work done by)} \]

\[ = 1\text{mol}(8.314 \text{J/mol}\cdot\text{K})(773.15\text{K})\ln(20/10) = +4.456\text{kJ} \]

\[ W_{CD} = nRT_L \ln \left( \frac{V_D}{V_C} \right) \quad \text{(work done on)} \]

\[ = 1\text{mol}(8.314 \text{J/mol}\cdot\text{K})(473.15\text{K})\ln(0.5) = -2.727\text{kJ} \]

Adiabatic branches (B→C, D→A) (\(Q = 0\)):

\[ W_{BC} = -\Delta U_{BC} = -nC_v(T_c - T_B) = -(1\text{mol}) \left( \frac{3}{2} \right)(8.314 \text{J/mol}\cdot\text{K})(473.15 - 773.15)K = +3.741\text{kJ} \]

\[ W_{DA} = -\Delta U_{DA} = -nC_v(T_A - T_D) = -(1\text{mol}) \left( \frac{3}{2} \right)(8.314 \text{J/mol}\cdot\text{K})(773.15 - 473.15)K = -3.741\text{kJ} \]

Thus,
\[ W_{\text{net}} = 4.456kJ - 2.727kJ + 3.741kJ - 3.741kJ = +1.729kJ = +1.73kJ \]

(net work is done BY gas).

b) Now we calculate the heat transfers:

A→B: isothermal. \( Q_{AB} = W_{AB} = +4.456kJ \)

B→C: adiabatic. \( Q_{BC} = 0 \)

C→D: isothermal. \( Q_{CD} = W_{CD} = -2.727kJ \)

D→A: adiabatic. \( Q_{DA} = 0 \)

Thus,

\[ Q_{\text{absorbed}} = Q_{AB} = +4.456kJ = +4.46kJ \]

And the system releases heat during only the process C→D so that

\[ Q_{\text{release}} = Q_{CD} = -2.727kJ = -2.73kJ \]

d) The efficiency of this heat engine is

\[ e = \frac{|W_{\text{net}}|}{|Q_{\text{absorbed}}|} = \frac{1.729kJ}{4.456kJ} = 0.388 = 38.8\% \]

**Shorter Method:**

This is a Carnot cycle and its efficiency is given by:

\[ e = 1 - \frac{T_L}{T_H} = 1 - \frac{473.15K}{773.15K} = 38.8\% \text{ (same as before)} \]

Now, we need to calculate the net work done and it is given by the two isothermal branches:

\[ W_{\text{net}} = W_{AB} + W_{CD} = nRT_H \ln \left( \frac{V_B}{V_A} \right) + nRT_L \ln \left( \frac{V_D}{V_C} \right) \]

(Work done by the adiabatic branches (B→C and D→A) cancel out each other.)

From the adiabatic relation, \( TV^{\gamma-1} = \text{const} \), we can write:

\[ T_A V_A^{\gamma-1} = T_D V_D^{\gamma-1} \quad \text{and} \quad T_B V_B^{\gamma-1} = T_C V_C^{\gamma-1} \]

Dividing these two equations, we have

\[ \frac{T_B V_B^{\gamma-1}}{T_A V_A^{\gamma-1}} = \frac{T_C V_C^{\gamma-1}}{T_D V_D^{\gamma-1}} \]

Since \( T_A = T_B = T_H \) and \( T_C = T_D = T_L \), this ratios simplify to:
\( \frac{V_B}{V_A} = \frac{V_C}{V_D} = 2 \). Inserting these ratios back into the work equations, we have,

\[
W_{\text{net}} = nRT_H \ln(2) + nRT_L \ln(0.5) = 1 \text{mol} \left(8.314 \text{J/mol \cdot K}\right) \left[773.15 \text{K} - 473.15 \text{K}\right] \ln 2
\]

\[ W_{\text{net}} = 1.729 \text{kJ} \]

Then, we can use the definition of efficiency to get the absorbed heat:

\[
e = \frac{W_{\text{net}}}{|Q_H|} \rightarrow |Q_H| = \frac{W_{\text{net}}}{e} = \frac{1.729 \text{kJ}}{0.388} = 4.456 \text{kJ} \quad \rightarrow \quad Q_H = +4.456 \text{kJ}
\]

Finally, to calculate heat related, we use the relation:

\[
W_{\text{net}} = |Q_H| - |Q_L| \rightarrow |Q_L| = |Q_H| - W_{\text{net}} = 4.456 \text{kJ} - 1.729 \text{kJ} = 2.727 \text{kJ}
\]

\[ Q_L = -2.727 \text{kJ} \]

All these values match with the previous direct but longer calculations.
4. (25 pts)
a) One mole of a monoatomic gas is being compressed reversibly from an initial state \( (V_1 = 5.00 \, \text{L}, P_1 = 5.00 \times 10^5 \, \text{Pa}) \) to a final state \( (V_2 = 3.00 \, \text{L}, P_2 = 3.00 \times 10^5 \, \text{Pa}) \). Calculate the entropy change \( \Delta S \) for this reversible process.

b) What will the entropy change \( \Delta S \) be for the same ideal gas if the process is done irreversibly but with the same initial and final states as in part a)?

c) 10.0 g of water is heated slowly from 20\(^\circ\)C to its boiling point at 100\(^\circ\)C and all of it is converted into steam at 100\(^\circ\)C. What is the total entropy change \( \Delta S \) for this heating and vaporization process? \([ L_v = 22.6 \times 10^5 \, \text{J/g}, c_{water} = 4.186 \, \text{J/g} \cdot ^\circ\text{C} \])

a) For any reversible process, the change in entropy is given by:

\[
\Delta S = nC_v \ln \left( \frac{T_f}{T_i} \right) + nR \ln \left( \frac{V_f}{V_i} \right)
\]

We have the volume ratio and to get the temperature ratio, we can use the ideal gas law, we have

\[
\frac{PV}{T} = \text{const} \quad \Rightarrow \quad \frac{T_f}{T_i} = \frac{P_fV_f}{P_iV_i}
\]

Thus, we have \( (C_v = 3R / 2 \) for a monoatomic ideal gas)

\[
\Delta S_a = (1 \text{mole})(8.314 \, \text{J/mole} \cdot \text{K}) \left[ \frac{3}{2} \ln \left( \frac{P_fV_f}{P_iV_i} \right) + \ln \left( \frac{V_f}{V_i} \right) \right]
\]

\[
\Delta S_a = (8.314 \, \text{J/K}) \left[ \frac{3}{2} \ln \left( \frac{9}{25} \right) + \ln \left( \frac{3}{5} \right) \right] = -17.0 \, \text{J/K}
\]

The change of entropy is negative since the process is a compression.

b) Since entropy is a state variable and the initial and final states are the same as in part a), the change in entropy for a nonreversible process between the same state 1 to 2 is the same as in part a):

\[
\Delta S_b = \Delta S_a = -17.0 \, \text{J/K}
\]

c) In heating liquid water slowly for a small change in temperature dT, the infinitesimal heat absorbed by the water is given by:

\[
dQ_{\text{heating}} = mc_{\text{water}}dT
\]
Then, the infinitesimal change in entropy is 
\[ dS_{\text{heating}} = \frac{dQ_{\text{heating}}}{T}. \] 
For the full range of temperature change \([20^\circ C \rightarrow 100^\circ C]\), we have:

\[
\Delta S_{\text{heating}} = \int_{T_i}^{T_f} \frac{dQ_{\text{heating}}}{T} = \int_{T_i}^{T_f} mc_{\text{water}} \frac{dT}{T} = mc_{\text{water}} \ln \left( \frac{T_f}{T_i} \right) \quad \text{(temp has to be in K)}
\]

\[
\Delta S_{\text{heating}} = (10.0 \text{g})(4.186 \text{J/g} \cdot \text{K}) \ln \left( \frac{373.15 \text{K}}{293.15 \text{K}} \right) = +10.10 \text{J/K} \quad \text{(heating is an entropy increasing process)}
\]

Now, the water vaporizes into steam at the boiling point, the heat of vaporization is absorbed at a fixed temperature. The increase in entropy is then given by:

\[
\Delta S_{\text{vaporize}} = \frac{mL_v}{T_{\text{boiling}}} = \frac{10.0 \text{g}(22.6 \times 10^2 \text{J/g})}{(373.15 \text{K})} = +60.57 \text{J/K}
\]

So, the TOTAL entropy increase is the sum of the two,

\[
\Delta S_{\text{tot}} = 10.10 \text{J/K} + 60.57 \text{J/K} = +70.7 \text{J/K}
\]