Chemistry 304 - Problem Set 2 - Detailed Solutions

1. **Aerogels are among the lightest materials known with densities about $0.07\,\mathrm{g\,cm^{-3}}$ and specific heat capacity $c_V = 2\,\mathrm{J\,g^{-1}\,K^{-1}}$ (assumed constant). Calculate the change in entropy, in $\mathrm{J\,K^{-1}}$, when $100\,\mathrm{g}$ of aerogel are encased in a rigid container and slowly heated from $T_1\,^\circ\mathrm{C}$ to $T_2\,^\circ\mathrm{C}$.**

   In class, we generally use molar quantities for heat capacities and other thermodynamic values, however in practice, especially for solids and liquids with complex chemical structures, it is easier to use specific values. Specific values divide heat capacity or other thermodynamic quantities by the mass of a substance rather than the number of moles.

   In this case, the system is slowly heated, implying the process is reversible, so the given process can be used directly to calculate the heat required in the entropy formula. The aerogel is in a rigid container so the volume is held constant during the heating process, that is $dq_V = c_V dT$. Putting all this together then gives (with m the mass of the aerogel)

$$\begin{aligned} dS &= \frac{dq_{rev}}{T} = \frac{mc_V\,dT}{T} \quad \text{integrating gives} \\ \Delta S &= \int_{T_i}^{T_f} mc_V \frac{dT}{T} = mc_V \int_{T_i}^{T_f} \frac{dT}{T} = mc_V \ln\left(\frac{T_f}{T_i}\right) \\ &= 100\,\mathrm{g} \times 2\,\mathrm{J\,g^{-1}\,K^{-1}} \times \ln\left(\frac{T_2 + 273.15\,\mathrm{K}}{T_1 + 273.15\,\mathrm{K}}\right) = 200 \ln\left(\frac{T_2 + 273.15}{T_1 + 273.15}\right)\,\mathrm{J\,K^{-1}}\ , \end{aligned}$$

   where in the second line c_V has been treated as a constant.

2. **An apparatus to determine the Joule coefficient consists of two insulated chambers. The first has volume $V_1\,\mathrm{L}$ and the second $V_2\,\mathrm{L}$. $3\,\mathrm{mol}$ of methane gas are placed in the first chamber and the second chamber is evacuated. A stopper is then removed and the gas expands to fill both chambers. Treating the gas as ideal, calculate $\Delta S_{\mathrm{universe}}$, in $\mathrm{J\,K^{-1}}$, for this process.**

   The apparatus is insulated so the process is adiabatic. This means no heat is exchanged with the surroundings, $q = q_{\mathrm{surr}} = 0$, so that $\Delta S_{\mathrm{surr}} = 0$ and $\Delta S_{\mathrm{universe}} = \Delta S$. Because the gas expands into a vacuum ($P_{ext} = 0$) no work is done, that is $dU = dq + dw = 0$ for the expansion. But for an ideal gas, $dU = C_V dT$, so $dU = 0$ implies $dT = 0$. The expansion is isothermal for the ideal gas. Unfortunately, the process is also irreversible, which means we have to find a reversible path between the same initial and final states in order to calculate the change in entropy. The system moves from (P_1, V_1, T) to $(P_2, V_1 + V_2, T)$ so consider a reversible, isothermal expansion from volume V_1 to volume $V_1 + V_2$, that is

$$\begin{aligned} dS &= \frac{dq_{rev}}{T} = \frac{C_V dT + P dV}{T} = nR\frac{dV}{V} \\ \Delta S &= nR \int_{V_1}^{V_1+V_2} \frac{dV}{V} = nR \ln\left(\frac{V_1 + V_2}{V_1}\right) \\ \Delta S_{\mathrm{universe}} &= 3\,\mathrm{mol} \times 8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}} \times \ln\left(\frac{V_1 + V_2}{V_1}\right) = 24.9435 \ln\left(\frac{V_1 + V_2}{V_1}\right)\,\mathrm{J\,K^{-1}}\ , \end{aligned}$$

   where in the first line $dT = 0$ because the process is isothermal, $dw = -PdV$ because only $P-V$ work is present and the process is reversible, and $P/T = nR/V$ because the gas is ideal. Also, be careful to note that the gas occupies both chambers after the expansion so the final volume is $V_1 + V_2$.

3. $25\,\text{mol}$ **of liquid water is swirled by a magnetic stir rod in an insulated beaker until its temperature rises from** $T_1\,^\circ\text{C}$ **to** $T_2\,^\circ\text{C}$**. Assuming the pressure is constant at** $1\,\text{atm}$ **and taking the heat capacity of water to be** $C_{P,m} = 75.5\,\text{J mol}^{-1}\,\text{K}^{-1}$ **and constant, calculate the change in entropy of the water.**

This is an example where irreversible work is converted to heat. The process is isobaric. We need to find a reversible path between the same initial and final states of the water, that is from (P, V_1, T_1) to (P, V_2, T_2). Consider the reversible, isobaric heating of the water from T_1 to T_2, that is

$$dS = \frac{dq_{rev}}{T} = \frac{C_P dT}{T} \quad \text{integrating gives}$$

$$\Delta S = nC_{P,m}\int_{T_i}^{T_f}\frac{dT}{T} = nC_{P,m}\ln\left(\frac{T_f}{T_i}\right)$$

$$= 25\,\text{mol} \times 75.5\,\text{J mol}^{-1}\,\text{K}^{-1} \times \ln\left(\frac{T_2 + 273.15\,\text{K}}{T_1 + 273.15\,\text{K}}\right) = 1887.5\ln\left(\frac{T_2 + 273.15\,\text{K}}{T_1 + 273.15\,\text{K}}\right)\,\text{J K}^{-1}\ ,$$

where in the second line $C_{P,m}$ was treated as a constant.

4. **In this question you will calculate the absolute standard entropy of carbon dioxide using experimental data. Upon heating at** $1\,\text{atm}$ **from** $T = 0\,\text{K}$**, solid carbon dioxide sublimes at** $T = 194.65\,\text{K}$ **with a molar enthalpy of sublimation,** $\Delta H_{sub} = 25.23\,\text{kJ mol}^{-1}$**. Near** $T = 0\,\text{K}$**, the heat capacity is well approximated by Debye theory which predicts**

$$C_{P,m}(T) = \frac{12\pi^4}{5}R\left(\frac{T}{\Theta_D}\right)^3$$

with a Debye temperature of $\Theta_D = 139.59\,\text{K}$**. This form can be used in the temperature range** $T = 0$ **to** $T = 15.52\,\text{K}$**. Using experimental heat capacities, it has already been determined that** $S^0_m(T = 194.65\,\text{K}) - S^0_m(T = 15.52\,\text{K}) = 68.274\,\text{J mol}^{-1}\,\text{K}^{-1}$**. For** $T > 194.65\,\text{K}$ **the heat capacity of carbon dioxide, in** $\text{J mol}^{-1}\,\text{K}^{-1}$**, is well approximated by the function**

$$C_{P,m}(T) = 21.64 + 0.06358T - 4.057\times10^{-5}T^2 + 9.700\times10^{-9}T^3\ .$$

Calculate the absolute standard molar entropy, S^0_m**, of carbon dioxide, in** $\text{J mol}^{-1}\,\text{K}^{-1}$ **at** $T_1\,\text{K}$**.**

Absolute standard entropies are obtained by reversibly heating a substance from $T = 0$ to a finite temperature under isobaric conditions at $1\,\text{atm}$, thus $dS = dq_{rev}/T = dH/T = nC_{P,m}dT/T$ so that $dS^0_m = c_{P,m}(T)dT/T$. In this case, the heat capacity function changes depending upon the temperature range, with the ranges in this case being $T = 0 \to 15.52\,\text{K}$, $T = 15.52\,\text{K} \to 194.65\,\text{K}$, and $T = 194.65\,\text{K} \to T_1\,\text{K}$. As well, T_1 is greater than the sublimation temperature so the solid carbon dioxide sublimes to a gas at $T = 194.65\,\text{K}$ creating an entropy change that also must be accounted for. Putting all this together then gives at a high level,

$$S^0_m(T_1) = S^0_m(T = 0\,\text{K}) + \Delta S^0_m(T = 0\,\text{K} \to 15.52\,\text{K}) + \Delta S^0_m(T = 15.52\,\text{K} \to 194.65\,\text{K})$$
$$+ \Delta S^0_m(\textit{sublimation}) + \Delta S^0_m(T = 194.65\,\text{K} \to T_1\,\text{K})\ .$$

The Third Law specifies $S^0_m(T = 0\,\mathrm{K}) = 0$, and in the question we are explicitly given $\Delta S^0_m(T = 15.52\,\mathrm{K} \rightarrow 194.65\,\mathrm{K}) = 68.274\,\mathrm{J\,mol^{-1}\,K^{-1}}$. Using the Debye heat capacity expression at low temperatures gives

$$\begin{aligned}\Delta S^0_m(T = 0\,\mathrm{K} \rightarrow 15.52\,\mathrm{K}) &= \int_0^{15.52} \frac{C_{P,m}(T)}{T} dT = \frac{12\pi^4}{5} \frac{R}{\Theta_D^3} \int_0^{15.52} T^2 dT \\ &= \frac{12\pi^4}{5} \frac{8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}}}{3} \left(\frac{15.52\,\mathrm{K}}{139.59\,\mathrm{K}} \right)^3 = 0.890508\,\mathrm{J\,mol^{-1}\,K^{-1}} \ .\end{aligned}$$

The entropy change of sublimation can be calculated using the enthalpy for the phase change, that is

$$\Delta S^0_m(\mathit{sublimation}) = \frac{\Delta H_{sub}}{T_{sub}} = \frac{25.23\,\mathrm{kJ\,mol^{-1}}}{194.65\,\mathrm{K}} = 129.61726\,\mathrm{J\,mol^{-1}\,K^{-1}} \ .$$

The final component of the calculation uses the heat capacity expression at the higher temperature range, that is

$$\begin{aligned}\Delta S^0_m(T = 194.65\,\mathrm{K} \rightarrow T_1\,\mathrm{K}) &= \int_{194.65}^{T_1} \frac{C_{P,m}(T)}{T} dT \\ &= \int_{194.65}^{T_1} \left(\frac{21.64}{T} + 0.06358 - 4.057 \times 10^{-5} T + 9.700 \times 10^{-9} T^2 \right) dT \\ &= 21.64 \ln \left(\frac{T_1}{194.65} \right) + 0.06358(T_1 - 194.65) \\ &\quad - \frac{4.057 \times 10^{-5}}{2} (T_1^2 - 194.65^2) + \frac{9.700 \times 10^{-9}}{3} (T_1^3 - 194.65^3)\,\mathrm{J\,K^{-1}} \ ,\end{aligned}$$

Putting all these bits and pieces together then gives

$$\begin{aligned}S^0_m(T_1) &= 198.78177 + 21.64 \ln \left(\frac{T_1}{194.65} \right) + 0.06358(T_1 - 194.65) \\ &\quad - \frac{4.057 \times 10^{-5}}{2} (T_1^2 - 194.65^2) + \frac{9.700 \times 10^{-9}}{3} (T_1^3 - 194.65^3)\,\mathrm{J\,K^{-1}} \ .\end{aligned}$$

5. **A cylinder filled with** $4\,\mathrm{mol}$ **of gaseous dimethyl ether is fitted with a frictionless piston held in place by locking pins. The gas is initially at a pressure of** $1\,\mathrm{atm}$ **with a volume of** $V_1\,\mathrm{L}$ **but the external pressure on the piston is much greater than** $1\,\mathrm{atm}$**. The entire system is immersed in a large water bath held at a constant temperature. The locking pins are released and the piston compresses the gas. Eventually the system equilibrates when the pressure is the same on both sides of the piston, at which point the volume of the gas is found to be** $V_2\,\mathrm{L}$**. Calculate** $\Delta S_{\mathrm{universe}}$ **for this process, in** $\mathrm{J\,K^{-1}}$**, treating dimethyl ether as a van der Waals gas with** $a = 8.073\,\mathrm{L^2\,atm\,mol^{-2}}$**,** $b = 0.07246\,\mathrm{L\,mol^{-1}}$**, and** $C_{P,m} = 65.57\,\mathrm{J\,mol^{-1}\,K^{-1}}$**.**

The entropy change for the system and for the surroundings need to be calculated individually. The process is also irreversible. Let's begin with the entropy change for the system. Because the process is irreversible, we need to construct a reversible path between the same initial and final states of the gas, that is from (P_1, V_1, T) to (P_2, V_2, T); the gas stays at the same

temperature because the system is immersed in a large water bath, making an isothermal process. Let's consider the isothermal compression of a van der Waals at temperature T from volume V_1 to V_2, that is

$$\begin{aligned}
dS &= \frac{dq_{rev}}{T} = \frac{dU - dw_{rev}}{dT} = \frac{C_V dT + \frac{n^2 a}{V^2} dV + P dV}{T} \\
&= \frac{\frac{n^2 a}{V^2} dV + \left(\frac{nRT}{V-nb} - \frac{n^2 a}{V^2}\right) dV}{T} = nR \frac{dV}{V - nb} \quad \text{integrating gives} \\
\Delta S &= nR \ln\left(\frac{V_2 - nb}{V_1 - nb}\right) \\
&= 4\,\text{mol} \times 8.3145\,\text{J mol}^{-1}\,\text{K}^{-1} \times \ln\left(\frac{V_2 - 4\,\text{mol} \times 0.07246\,\text{L mol}^{-1}}{V_1 - 4\,\text{mol} \times 0.07246\,\text{L mol}^{-1}}\right) \\
&= 33.258 \ln\left(\frac{V_2 - 0.28984}{V_1 - 0.28984}\right)\ \text{J K}^{-1}\ ,
\end{aligned}$$

with V_1 and V_2 in L units. Since only $P-V$ work is present and the process is reversible, $P_{ext} = P$ as well as the van der Waals equation were used in the first line, as well as $(\partial U/\partial V)_T = n^2 a/V^2$ for a van der Waals gas. The process is isothermal so $dT = 0$.

To calculate the entropy change for the surroundings, we require the temperature of the surroundings and the heat flow in the process. Given the initial condition of the gas, and rearranging the van der Waals equation of state, the temperature of the gas (and hence the temperature of the water bath) is

$$\begin{aligned}
T &= \left(\frac{V_1 - nb}{nR}\right)\left(P_1 + \frac{n^2 a}{V_1^2}\right) \\
&= \left(\frac{V_1 - 4\,\text{mol} \times 0.07246\,\text{L mol}^{-1}}{4\,\text{mol} \times 0.082057\,\text{L atm mol}^{-1}\,\text{K}^{-1}}\right)\left(1\,\text{atm} + \frac{4^2\,\text{mol}^2 \times 8.073\,\text{L}^2\,\text{atm mol}^{-2}}{V_1^2}\right) \\
&= \left(\frac{V_1 - 0.28984}{0.328228}\right)\left(1 + \frac{129.168}{V_1^2}\right)\ \text{K}\ ,
\end{aligned}$$

with V_1 and V_2 in L. Use the First law to find the heat flow in the process, that is

$$\begin{aligned}
dU &= dq + dw \\
C_V dT + \frac{n^2 a}{V^2} dV &= dq - P_{ext} dV \\
dq &= \left(\frac{n^2 a}{V^2} + P_{ext}\right) dV \quad \text{integrating gives} \\
q &= \int_{V_1}^{V_2} \left(\frac{n^2 a}{V^2} + P_{ext}\right) dV = n^2 a \left(\frac{1}{V_1} - \frac{1}{V_2}\right) + P_{ext}(V_2 - V_1) \\
&= 129.168 \left(\frac{1}{V_1} - \frac{1}{V_2}\right) + P_{ext}(V_2 - V_1)\,\text{L atm}\ ,
\end{aligned}$$

in which P_{ext} is constant in the process, $dT = 0$, and $(\partial U/\partial V)_T = n^2 a/V^2$ for a van der Waals gas. Now, P_{ext} is the same as the final pressure of the gas, which using the van der Waals equation is

$$P_{ext} = \frac{nRT}{V_2 - nb} - \frac{n^2 a}{V_2^2} = \frac{0.328228T}{V_2 - 0.28984} - \frac{129.168}{V_2^2}\,\text{atm}\ ,$$

with V_2 in L. The heat lost by the system is gained by the surroundings, and we treat this heat as being delivered reversibly there with an isothermal process, giving

$$\begin{aligned}\Delta S_{\text{surr}} &= \frac{q_{rev,surr}}{T_{\text{surr}}} = -\frac{q}{T} \\ &= -\frac{1}{T}\left[129.168\left(\frac{1}{V_1}-\frac{1}{V_2}\right)+P_{ext}(V_2-V_1)\right]\,\text{L atm K}^{-1} \\ &= -\frac{101.325}{T}\left[129.168\left(\frac{1}{V_1}-\frac{1}{V_2}\right)+P_{ext}(V_2-V_1)\right]\,\text{J K}^{-1}\ ,\end{aligned}$$

with P_{ext} and T determined from the equations given above. The entropy change in the universe is then the sum of the contributions from the system and surroundings,

$$\Delta S_{\text{universe}} = \Delta S + \Delta S_{\text{surr}}\ ,$$

with the system and surroundings values taken from the equations given above. Notice that $\Delta S_{\text{universe}} > 0$, as it should be, indicating the original process was irreversible.

6. **Show that for a reversible, adiabatic process with an ideal gas involving only $P-V$ work, PV^γ is constant, where $\gamma = C_{P,m}/C_{V,m}$ (assuming constant heat capacities).** *Hint: for fixed n, consider a change of state from (P_1,V_1) to (P_2,V_2) and show that $P_1V_1^\gamma = P_2V_2^\gamma$, implying that PV^γ is constant throughout the process.* **Aside: from this relation (using the ideal gas law) it also follows that $TV^{R/C_{V,m}}$ is constant, and $TP^{-R/C_{P,m}}$ is constant.**

For a reversible process, $P_{ext} = P$ so $dw = -PdV$ assuming only $P-V$ work is present. As well, for an ideal gas $dU = C_V dT$ since $(\partial U/\partial V)_T = 0$, and $dq = 0$ for an adiabatic process. Putting all these pieces together, and considering an adiabatic expansion from (P_1,V_1,T_1) to (P_2,V_2,T_2), the First Law can be written

$$\begin{aligned}C_V dT &= -PdV = -\frac{nRT}{V}dV \\ \frac{dT}{T} &= -\frac{R}{C_{V,m}}\frac{dV}{V} \quad \text{integrating gives} \\ \int_{T_1}^{T_2}\frac{dT}{T} &= -\frac{R}{C_{V,m}}\int_{V_1}^{V_2}\frac{dV}{V} \\ \ln\left(\frac{T_2}{T_1}\right) &= -\frac{R}{C_{V,m}}\ln\left(\frac{V_2}{V_1}\right) \\ \frac{T_2}{T_1} &= \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_{V,m}}} \\ T_2V_2^{\frac{R}{C_{V,m}}} &= T_1V_1^{\frac{R}{C_{V,m}}} \\ P_2V_2V_2^{\frac{R}{C_{V,m}}} &= P_1V_1V_1^{\frac{R}{C_{V,m}}} \\ P_2V_2^\gamma &= P_1V_1^\gamma\ ,\end{aligned}$$

in which $C_{V,m}$ has been considered constant, the ideal gas law was used to transform T_2/T_1 to P_2V_2/P_1V_1, and

$$\gamma = 1+\frac{R}{C_{V,m}} = \frac{C_{V,m}+R}{C_{V,m}} = \frac{C_{P,m}}{C_{V,m}}\ ,$$

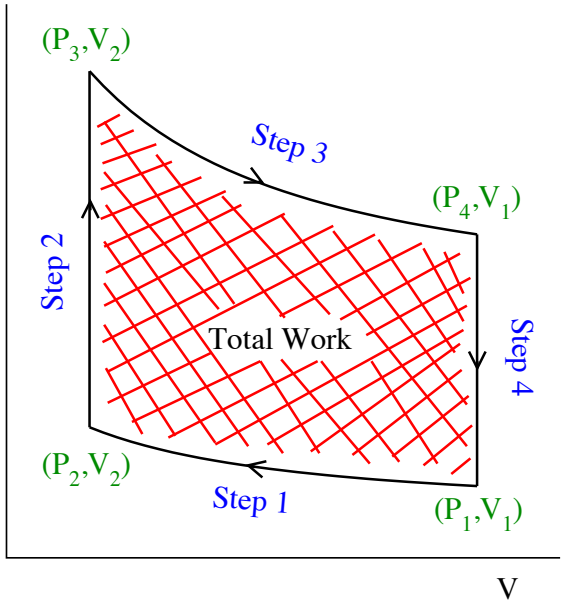
remembering that for an ideal gas, $C_{P,m} = C_{V,m} + R$. Since P_1 and P_2 are arbitrary, the equality above must be satisfied during the entire process. In other words, for a reversible, adiabatic process involving an ideal gas and only $P - V$ work, PV^γ is a constant.

7. **Many gasoline, internal combustion, piston engines are based on the Otto cycle which can be broken down into four steps:**
   1) **A fuel-air mixture in a cylinder fitted with a piston is compressed rapidly from volume V_1 and pressure P_1 to a volume V_2 and pressure P_2, at which point a spark ignites the fuel-air mixture.**
   2) **The fuel burns very quickly, increasing the pressure from P_2 to P_3 in a fixed volume V_2.**
   3) **This increase in pressure forces the piston outward, increasing the volume back to the original value V_1 and reducing the pressure to P_4.**
   4) **At this point, a valve opens to reduce the pressure from P_4 to P_1 while keeping the volume fixed at V_1.**

   Note that a subsequent stroke is needed to expel the exhaust gases and fill the chamber with new fuel-air mixture to return the system to its starting point. However, we can ignore this part of the cycle as well as the details of Step 4 because the work involved with them is small. In an engine, the cycle is very fast so Steps 1 and 3 can be approximated as adiabatic. As well, the fuel-air mixture is often approximated as an ideal gas.

a) **On a labelled $P - V$ diagram, sketch the Otto cycle, indicating the values of P and V at the beginning and end of each of the four Steps. Label the four Steps, putting arrows to show the direction the cycle is traversed, and show graphically the total work done by the cycle.**

The graph on the right shows the four Steps on a $P - V$ diagram, with the pressures and volumes indicated on the vertices. The total work is just the are enclosed by the cycle.



b) **Assuming the Otto cycle were performed reversibly, find expressions for q and w for Steps 1–3 in terms of the appropriate pressures, volumes, and $C_{V,m}$, the latter of which can be approximated as constant throughout the cycle.** *Note that in principle the number of moles of gas could change in Step 2 depending upon the stoichiometry of the combustion reaction of the fuel. However, the fuel typically is in low concentration so ignore this effect and treat the number of moles as approximately constant in Steps 1–3.*

Consider heat first. Since Steps 1 and 3 are adiabatic, $q_1 = 0$ and $q_3 = 0$. Step 2 is an isochoric expansion, so $dq_V = C_V dT$ which upon integration (treating C_V and n as constant) yields

$$q_2 = C_V(T_3 - T_2) = \frac{C_V}{nR}(P_3V_2 - P_2V_2) = \frac{C_{V,m}}{R}(P_3V_2 - P_2V_2) \ ,$$

in which the ideal gas law was used to transform the equation. Now consider work. Since only $P-V$ work is present, and since Step 2 is isochoric, $w_2 = 0$. Since Steps 1 and 3 are adiabatic, $dU = dw$ so $w = \Delta U$. For an ideal gas, $dU = C_V dT$ so with constant heat capacity, $\Delta U = C_V \Delta T$. Applying this each for Steps 1 and 3 gives

$$w_1 = C_V(T_2 - T_1) = \frac{C_{V,m}}{R}(P_2V_2 - P_1V_1) \ ,$$
$$w_3 = C_V(T_4 - T_3) = \frac{C_{V,m}}{R}(P_4V_1 - P_3V_2) \ .$$

c) **Using the results from part b), show that the efficiency of the reversible Otto cycle is**

$$\eta = \frac{|w|}{|q_h|} = 1 - \frac{1}{r^{\gamma-1}} \ ,$$

in which q_h is the heat entering the cycle in Step 2, w is the total work of the cycle (from Steps 1 and 3), $r = V_1/V_2$ is the compression ratio, and $\gamma = C_{P,m}/C_{V,m}$ is the ratio of heat capacities. Show that this efficiency is the same as that for a Carnot engine. Is this expected? *Note: the result of Question 6 may prove helpful.*

Here $q_h = q_2$ and $w = w_1 + w_3$ from part b), and since $q_h > 0$ and $w < 0$, we have

$$\begin{aligned}
\eta &= -\frac{w_1 + w_3}{q_2} \\
&= -\frac{\frac{C_{V,m}}{R}(P_2V_2 - P_1V_1 + P_4V_1 - P_3V_2)}{\frac{C_{V,m}}{R}(P_3V_2 - P_2V_2)} \\
&= \frac{(P_3 - P_2)V_2 - (P_4 - P_1)V_1}{(P_3 - P_2)V_2} \\
&= 1 - \frac{(P_4 - P_1)V_1}{(P_3 - P_2)V_2} \ .
\end{aligned}$$

But Steps 1 and 3 are reversible, adiabatic processes involving only $P-V$ work using an ideal gas so from Question 6, we know that for Step 1, $P_1V_1^\gamma = P_2V_2^\gamma$, or with some rearrangement, $P_1V_1 = P_2V_2(V_2/V_1)^{\gamma-1}$. By a similar argument, $P_4V_1 = P_3V_2(V_2/V_1)^{\gamma-1}$. Using these relations in the expression for η then gives

$$\begin{aligned}
\eta &= 1 - \frac{(P_3 - P_2)V_2\left(\frac{V_2}{V_1}\right)^{\gamma-1}}{(P_3 - P_2)V_2} \\
&= 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1} = 1 - \frac{1}{r^{\gamma-1}} \ ,
\end{aligned}$$

with $r = V_1/V_2$ and $\gamma = C_{P,m}/C_{V,m}$.

To show that the efficiency formula is that same as that for the Carnot cycle, we need to write it as $\eta = 1 - T_c/T_h$, where T_c and T_h are the cold and hot bath temperatures, respectively. Now, for the Otto cycle, the heat transfer into the system occurs during Step 2, so the hot temperature, T_h, is the temperature at the end of Step 2, where the pressure and volume are (P_3, V_2). During the adiabatic expansion in Step 3, the gas cools, reaching the coldest temperature at the end of this step, where the pressure and volume are (P_4, V_1). At this point the gas is expelled from the cylinder, so the temperature at the end of Step 3 is the cold

temperature, T_c. We also know that (P_3, V_2) and (P_4, V_1) are linked by a reversible, adiabatic process involving an ideal gas, so from Question 6, $TV^{R/C_{V,m}}$ is constant during the entire process, that is $T_h V_2^{R/C_{V,m}} = T_c V_1^{R/C_{V,m}}$. Use this last result in the formula for the Otto cycle efficiency,

$$\eta = 1 - \frac{1}{r^{\gamma-1}} = 1 - \frac{V_2}{V_1}^{R/C_{V,m}} = 1 - \frac{T_c}{T_h} \ ,$$

remembering that $\gamma - 1 = R/C_{V,m}$. This shows that the efficiency for the Otto cycle is the same as that for the Carnot cycle. This is expected because, as noted in class and argued in detail in the Appendix of the notes, all reversible heat engines have the same efficiency. The key is that all processes in the cycle must be performed reversibly.

d) **For a typical engine, $\gamma \approx 1.3$ and $r \approx 10$. Use the formula from part c) to calculate the efficiency. Do you expect this to be the efficiency of an actual gasoline engine? Please justify your response.**

Using the efficiency formula from part c) gives

$$\eta = 1 - \frac{1}{10^{1.3-1}} = 0.50 \ .$$

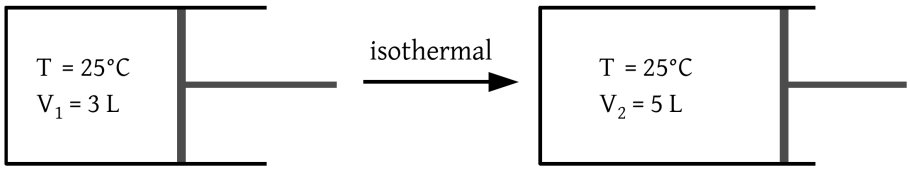
This is the theoretical maximum efficiency, assuming the engine has no losses due to friction, and that all processes are performed reversibly. For real engines, there will be losses due to irreversible processes so the expected efficiency will be less than 50%.

e) **The result of part c) shows that the compression ratio is the main design characteristic that limits engine efficiency. Gasoline engines typically have $r \approx 10$ but diesel engines (which use a cycle similar to the Otto cycle except they inject fuel directly into the cylinder at the end of the compression stroke) typically have $r \approx 15 - 23$, making them in general more efficient. Why, in practice, cannot a typical gasoline engine be designed with a compression ratio comparable to a diesel engine?**

During the compression stroke (Step 1), the temperature of the gas increases. Using the relation from Question 6, $T_2 = T_1(V_1/V_2)^{R/C_{V,m}} = T_1 r^{\gamma-1}$. Using the estimated values from part d) gives $T_2 = 10^{0.3} T_1 = 2T_1$. So, if the fuel-air mixture starts at about $T_1 = 300\,\mathrm{K}$, at the end of the compression cycle, the mixture is about $T_2 = 600\,\mathrm{K}$. With a compression ratio $r = 20$, $T_2 = 740\,\mathrm{K}$. At such high temperatures, the fuel-air mixture can spontaneously combust before the compression cycle is complete. In other words, the fact the cylinder is filled with a self-combusting fuel-air mixture limits the temperature at the end of the compression stroke, and hence limits r. In a diesel engine, only air is compressed so it can withstand a larger increase in temperature. At the end of the compression stroke, the temperature is high enough to cause spontaneous combustion of fuel, so that's why fuel is injected into the cylinder at that end of the stroke. The fuel spontaneously combusts, pushing the piston outward. The high temperature causes combustion so no spark plugs are needed in a diesel engine.

8. **At the Vancouver Flea Market you meet a person selling a device they claim will solve the world's energy problems. Using only about 3 moles of ammonia, the device expands the gas from $3\,\mathrm{L}$ to $5\,\mathrm{L}$, using a special (patented) series of chambers, and does $8\,\mathrm{kJ}$ of work in the process. The whole device is in contact with room temperature air ($T = 25\,^\circ\mathrm{C}$) and stays at this temperature the entire time. You are suspicious about this claim. Estimate q, ΔU, and ΔS for this expansion process treating ammonia as a van der Waals gas with constants $C_{V,m} = 26.75\,\mathrm{J\,mol^{-1}\,K^{-1}}$, $a = 4.17\,\mathrm{L^2\,atm\,mol^{-2}}$ and $b = 0.0371\,\mathrm{L\,mol^{-1}}$. Are the claims about the device substantiated?**

The expansion process is shown below where we are told the process is isothermal and that the system does 8 kJ of work on the surroundings so $dT = 0$, and $w = -8000\,\mathrm{J}$.



Begin by finding the change in internal energy, starting with the general expression and remembering that for a van der Waals gas, $(\partial U/\partial V)_T = n^2a/V^2$, that is

$$dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = \frac{n^2 a}{V^2} dV \quad \text{integrating gives}$$

$$\Delta U = n^2 a \int_{V_1}^{V_2} \frac{1}{V^2} dV = -n^2 a \left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$= -(3\,\mathrm{mol})^2 \times 4.17\,\mathrm{L}^2\,\mathrm{atm\,mol}^{-2} \left(\frac{1}{5\,\mathrm{L}} - \frac{1}{3\,\mathrm{L}}\right) = 5.00\,\mathrm{L\,atm} = 507\,\mathrm{J}\ .$$

Since $\Delta U = q + w$ then $q = \Delta U - w = 507\,\mathrm{J} - (-8000\,\mathrm{J}) = 8507\,\mathrm{J}$. The heat from a reversible expansion is needed to calculate ΔS and since we are not told explicitly that the process is reversible, we should not assume so *a priori*. Thus, consider the reversible, isothermal expansion of the van der Waals gas from 3 L to 5 L at $T = 25\,^\circ\mathrm{C} = 298\,\mathrm{K}$. This is precisely the same process used in the first part of Question 5, which showed that

$$\Delta S = nR \ln\left(\frac{V_2 - nb}{V_1 - nb}\right)$$

$$= 3\,\mathrm{mol} \times 8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}} \ln\left(\frac{5\,\mathrm{L} - 3\,\mathrm{mol} \times 0.0371\,\mathrm{L\,mol^{-1}}}{3\,\mathrm{L} - 3\,\mathrm{mol} \times 0.0371\,\mathrm{L\,mol^{-1}}}\right) = 13.12\,\mathrm{J\,K^{-1}}\ .$$

Are the claims about the device substantiated? There are several ways one could answer this. One way is by looking at work. For a reversible, isothermal process, $q_{rev} = T\Delta S = 3911\,\mathrm{J}$, so $w_{rev} = \Delta U - q_{rev} = 507 - 3911 = -3403\,\mathrm{J}$. Recall that w_{rev} is the maximum amount of energy a system can provide as work. However, the device supposedly provides 8000 J of energy as work which is more than twice the amount of w_{rev}. This is not possible. Actually, strictly speaking, it is not possible for the gas expansion alone to produce this much work. If the device truly performed 8000 J of work then it must have an auxiliary power source, different from the gas expansion, providing the extra energy. As an alternative way of verifying the claim, one could examine $\Delta S_{\mathrm{universe}}$ for the device by taking its data at face value. The heat for the surroundings is the negative of that for the system, so $q_{\mathrm{surr}} = -q = -8507\,\mathrm{J}$ and $\Delta S_{surr} = -8507\,\mathrm{J}/298\,\mathrm{K} = -28.5\,\mathrm{J\,K^{-1}}$. This gives $\Delta S_{univ} = \Delta S_{surr} + \Delta S = -28.5 + 13.1 = -15.4\,\mathrm{J\,K^{-1}}$. The entropy change for the universe is negative and this violates the Second Law of thermodynamics, and therefore is not possible.

9. **In our so-called "modern" world, cars are powered by internal combustion engines while homes and buildings are heated with electric baseboard heaters. Why are these poor ideas from an energy management viewpoint? Using sound thermodynamic arguments, how would you improve the situation (please justify your responses)?**

   As shown by Question 7, internal combustion engines have efficiencies of less than about 50%, meaning more than half of the energy in the gasoline exits the tailpipe, without being converted to work to power a car. In general, using heat engines to generate work is inefficient is one wants to have significant conversion to work. Electrical motors are not heat engines so are not constrained by the Carnot efficiency. In principle, the only losses in an electric motor are due to frictional (including resistive) losses within the components, so efficiencies can be quite high. So, from an energy management point of view, electric vehicles are far better than ones powered by combustion engines, assuming the electrical power to charge batteries in these vehicles is obtained by non-heat-engine means.

   When considering building heating, electric baseboard heaters use resistive components to convert, with essentially 100% efficiency, electrical power to heat. From a thermodynamic point of view, one is converting useful energy (that could in principle be used for work with 100% efficiency) to less useful energy (heat has a limited efficiency for doing work). This is not ideal. It would be much better to use the electricity to power a heat pump. Work can be used to maximum effect and transfer much more energy to heat a building. Each kilojoule of work supplied to a heat pump transfers multiple kilojoules of heat, much more efficient than an electric baseboard heater. Given that the efficiency of heat pumps increases the closer the temperatures between the hot and cold reservoirs, one good way to heat a building is to have insulated tanks of water that are heated during the summer, and then used as a heat reservoir during the winter for heat pumps. This creates a hot reservoir with a temperature very close to a building's temperature, thereby maximizing heat pump efficiency. Many kilojoules of heat could then be transferred into a building from the reservoir, using as little electrical work as possible.