

1.(15%) 2.25 moles of an ideal gas with $C_{V,m} = 3/2 R$ undergoes the transformations described in the following list from an initial state described by $T = 310 \text{ K}$. and $P = 1.00 \text{ bar}$. Calculate q , w , ΔU , ΔH , and ΔS for each process.

- (a) The gas is heated to 675 K at a constant external pressure of 1.00 bar .
- (b) The gas is heated to 675 K at a constant volume corresponding to the initial volume.
- (c) The gas undergoes a reversible isothermal expansion at 310 K until the pressure is one third of its initial value.

2.(15%) Consider the reversible Carnot cycle with 1.25 mol of an ideal gas with $C_{V,m} = 5/2 R$ as the working substance. The initial isothermal expansion occurs at the hot reservoir temperature of $T_{hot} = 740 \text{ K}$ from an initial volume of 3.75 L (V_a) to a volume of 12.8 L (V_b). The system then undergoes an adiabatic expansion until the temperature falls to $T_{cold} = 310 \text{ K}$. The system then undergoes an isothermal compression and a subsequent adiabatic compression until the initial state described by $T_a = 740 \text{ K}$ and $V_a = 3.75 \text{ L}$ is reached.

- (a) Calculate V_c and V_d .
- (b) Calculate w for each step in the cycle and for the total cycle.
- (c) Calculate ε and the amount of heat that is extracted from the hot reservoir to do 1.00 kJ of work in the surroundings.

3.(15%) 3 mole of an ideal gas with $C_{V,m} = 3/2 R$ undergoes the transformations described in the following list. (Initial state $T = 298 \text{ K}$ and $P = 4.5 \text{ bar}$.)

Calculate q , w , ΔU , ΔH , and ΔS for each process.

- (a) The gas undergoes a reversible adiabatic expansion until the final pressure is one third its initial value.
- (b) The gas undergoes an adiabatic expansion against a constant external pressure of 1.50 bar until the final pressure is one third its initial value.
- (c) The gas undergoes an expansion against a constant external pressure of zero bar (free expansion) until the final pressure is equal to one third its initial value.

4.(15%) A gas sample behaves like the ideal gas containing 2 moles for which $C_{V,m} = 5/2 R$ undergoes the following reversible cyclical process from an initial state : $T = 275 \text{ K}$ and $P = 1.00 \text{ bar}$.

- (a) It is expanded reversibly and adiabatically until the volume triples.
- (b) It is reversibly heated at constant volume until T increases to 275 K .
- (c) The pressure is increased in an reversible isothermal compression until

pressure recover to 1.00bar

Calculate q , w , ΔU , ΔH , and ΔS and ΔS_{tot} for each process.

5.(20 %) The first law states that the energy of the universe is a constant ($\Delta U = q + w$) while the second law states that the entropy of the universe tends always towards a maximum ($\Delta S_{\text{tot}} = \Delta S + \Delta S_{\text{surr}} \geq 0$). Answer the following questions *only* based on the conditions it is provided.

- Assuming that the entropy change of the system is $\Delta S = \frac{q_{\text{rev}}}{T}$, determine the relationship of ΔS_{surr} in terms of q_{rev} and T . (3%)
- If only PV -work is considered, prove that the inequality of work ($dw_{\text{rev}} < dw_{\text{irr}}$) is always valid (e.g., expansion or compression). (5%)
- Prove $dq_{\text{rev}} > dq_{\text{irr}}$ based on $dw_{\text{rev}} < dw_{\text{irr}}$. (2%)
- Based on $dq_{\text{rev}} > dq_{\text{irr}}$ to prove the Clausius inequality, $dS \geq \frac{dq}{T_{\text{surr}}}$, where the equality holds only for reversible processes. (3%)
- Following (c) and (d) to prove that the entropy change of any irreversible process is always greater than zero in an isolated system. (3%)
- Assuming that the system is no longer isolated, i.e., the surroundings are a reservoir of energy and the heat entering the system is equal to the heat leaving the surroundings. Show that the Clausius inequality can be deduced to a more general expression for the 2nd law, i.e., $dS_{\text{tot}} = dS + dS_{\text{surr}} \geq 0$. (4%)

6.(20%) You wish to construct a fuel cell based on oxidation of a hydrocarbon fuel. The two choices for a fuel are methane and octane. Calculate the maximum work available through the combustion of these two hydrocarbons, on a per mole and a per gram basis at 298.15 K and 1 bar pressure.

Useful thermodynamic data are the following:

	CH ₄ (g)	C ₈ H ₁₈ (l)	CO ₂ (g)	H ₂ O(l)	O ₂ (g)
ΔH_c^0 /kJ mol ⁻¹	-891	-5471	—	—	—
S_m^0 /J K ⁻¹ mol ⁻¹	186.3	361.1	213.8	70.0	205.2

Are there any other factors that should be taken into account in making a decision between these two fuels?