The Second Law of Thermodynamics & Entropy

Exercise 1:

State the two classical formulations of the Second Law of Thermodynamics and explain what each implies about the direction of natural processes.

1) State the **Clausius Statement** and give one physical example that illustrates it.
2) State the **Kelvin–Planck Statement** and explain why a 100% efficient heat engine is impossible.
3) A textbook states: *"The First Law tells us what is possible; the Second Law tells us what actually happens."* Do you agree? Justify with a concrete example.

Exercise 2:

For each of the following processes, state whether it is **spontaneous**, **non-spontaneous**, or **impossible**, and justify your answer using the Second Law:

a) Heat flows from a hot metal rod at $T_1 = 80°\text{C}$ to a cold liquid at $T_2 = 20°\text{C}$.

b) Two gases, initially separated by a membrane, mix spontaneously after the membrane is removed.

c) The mixed gases from (b) spontaneously separate back into their original containers.

d) A refrigerator transfers heat from cold food to a warm room.

Exercise 3:

Entropy S is a fundamental thermodynamic state function introduced by Clausius. For a **reversible** transformation, the entropy change of the system is defined as:

$$dS_{\text{sys}} = \frac{\delta Q_{\text{rev}}}{T_{\text{sys}}} \implies \Delta S_{\text{sys}} = \int_{\text{initial}}^{\text{final}} \frac{\delta Q_{\text{rev}}}{T_{\text{sys}}}$$

1) List the three fundamental properties of entropy as a state function. For each property, state one practical consequence.
2) A system undergoes a complete cyclic transformation (returns to its exact initial state). What is ΔS_{sys} for this cycle? Does this imply the process was reversible? Explain.
3) Distinguish carefully between ΔS_{ext}, $S_{\text{exchanged}}$, and S_{created}. Which of these are state functions?

Exercise 4:

One mole of an ideal gas undergoes a **reversible isothermal expansion** at $T = 300\,\mathrm{K}$ from $V_1 = 10\,\mathrm{L}$ to $V_2 = 40\,\mathrm{L}$. Recall that for this process:

$$\Delta S_{\text{sys}} = nR\ln\left(\frac{V_2}{V_1}\right)$$

1) Calculate ΔS_{sys}.
2) Calculate ΔS_{ext}, given that the surroundings are also at $T = 300\,\mathrm{K}$.
3) Calculate $\Delta S_{\text{universe}}$. Is this result consistent with the process being reversible?

Exercise 5:

Two moles of an ideal monatomic gas ($C_v = \frac{3}{2}R$) are heated **reversibly at constant volume** from $T_1 = 250\,\mathrm{K}$ to $T_2 = 500\,\mathrm{K}$.

1) Calculate Q_{rev} for this process.
2) Calculate ΔS_{sys} using:
$$\Delta S_{\text{sys}} = nC_v\ln\left(\frac{T_2}{T_1}\right)$$
3) Is ΔS_{sys} positive or negative? Interpret this physically in terms of molecular disorder.

Exercise 6:

One mole of an ideal gas ($\gamma = 5/3$) undergoes a **reversible adiabatic expansion** from state A: ($T_A = 400\,\mathrm{K}$, $V_A = 5\,\mathrm{L}$) to $V_B = 20\,\mathrm{L}$. Recall: $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$.

1) Calculate the final temperature T_B.
2) Calculate ΔS_{sys} and justify your result *without calculation* from the definition of a reversible adiabatic process.
3) If the same expansion were instead performed as a **free expansion into vacuum** (irreversible), what would ΔS_{sys} be? Is it positive, negative, or zero? Explain.

Exercise 7:

One mole of an ideal gas undergoes an **irreversible isothermal expansion** at $T = 300\,\mathrm{K}$ against a constant external pressure $P_{\text{ext}} = 1\,\mathrm{atm}$. The initial pressure is $P_1 = 5\,\mathrm{atm}$ and the final pressure is $P_2 = 1\,\mathrm{atm}$. Given: $R = 8.314\,\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$.

1) Calculate the irreversible work W_{irr} done by the gas against P_{ext}.
2) Using the First Law, calculate Q_{irr}.
3) Calculate ΔS_{sys}. Is ΔS_{sys} path-dependent? Justify your approach.
4) Calculate $\Delta S_{\text{ext}} = -Q_{\text{irr}}/T$.
5) Calculate $S_{\text{created}} = \Delta S_{\text{universe}}$. What does this value indicate about the irreversibility of the process?

Exercise 8:

Recall the **entropy balance equation**:

$$\Delta S_{\text{sys}} = S_{\text{exchanged}} + S_{\text{created}}, \qquad \text{where} \quad S_{\text{exchanged}} = \frac{Q}{T_{\text{ext}}}, \quad S_{\text{created}} \geq 0.$$

A gas inside a rigid container absorbs $Q = 500\,\text{J}$ of heat *irreversibly* from a thermal reservoir at $T_{\text{ext}} = 600\,\text{K}$. The gas temperature is also $600\,\text{K}$.

1) Calculate ΔS_{sys}, $S_{\text{exchanged}}$, and S_{created}.
2) What does the value of S_{created} indicate about this process?

Exercise 9:

An ideal gas is heated **irreversibly at constant pressure**. It absorbs $Q = 2000\,\text{J}$ from a reservoir at $T_{\text{ext}} = 500\,\text{K}$, and its temperature increases from $T_1 = 300\,\text{K}$ to $T_2 = 500\,\text{K}$.

1) Calculate $S_{\text{exchanged}} = Q/T_{\text{ext}}$.
2) Explain why ΔS_{sys} is **not** calculated using $Q_{\text{irr}}/T_{\text{ext}}$, even though Q_{irr} is known.
3) Given $\Delta S_{\text{sys}} = nC_p \ln(T_2/T_1) = 6.5\,\text{J}\cdot\text{K}^{-1}$, calculate S_{created} and comment on the result.

Exercise 10:

The **entropy of mixing** for ideal gases at constant temperature and total pressure is:

$$\Delta S_{\text{mix}} = -R \sum_i n_i \ln x_i$$

where $x_i = n_i/n_{\text{total}}$ is the mole fraction of component i.
2 mol of N_2 and 3 mol of O_2, both at 298 K and 1 atm, are mixed in a thermally insulated container.

1) Calculate the mole fractions $x(N_2)$ and $x(O_2)$.
2) Calculate ΔS_{mix}.
3) Is ΔS_{mix} positive or negative? Interpret physically.
4) Show algebraically that for *any* binary mixture with $0 < x_1 < 1$, ΔS_{mix} is always positive. What does this imply about the spontaneity of ideal gas mixing?

Exercise 11:

The **Third Law of Thermodynamics** states that the entropy of any pure substance in the form of a perfect crystal is zero at $T = 0\,\mathrm{K}$.
Using the following standard molar entropies at 298 K:

$$S^\circ(\mathrm{N_2, g}) = 191.6\,\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}, \quad S^\circ(\mathrm{H_2, g}) = 130.7\,\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}, \quad S^\circ(\mathrm{NH_3, g}) = 192.5\,\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$$

for the Haber process:

$$\mathrm{N_2(g)} + 3\,\mathrm{H_2(g)} \longrightarrow 2\,\mathrm{NH_3(g)}, \qquad \Delta H^\circ_{\mathrm{rxn}} = -92\,\mathrm{kJ{\cdot}mol^{-1}}$$

1) Calculate $\Delta S^\circ_{\mathrm{rxn}}$.
2) Calculate $\Delta S^\circ_{\mathrm{universe}}$ at $T = 298\,\mathrm{K}$.
3) Determine the crossover temperature T^* at which $\Delta S_{\mathrm{universe}} = 0$, assuming ΔH° and $\Delta S^\circ_{\mathrm{sys}}$ are temperature-independent.
4) Comment on the practical implications: the industrial Haber process operates near $T \approx 700\,\mathrm{K}$. What does your result suggest about the thermodynamic spontaneity at that temperature?

Exercise 12:

A **Carnot engine** operates between a hot reservoir at $T_H = 600\,\mathrm{K}$ and a cold reservoir at $T_C = 300\,\mathrm{K}$, absorbing $Q_H = 4000\,\mathrm{J}$ per cycle.

1) Calculate the thermal efficiency η of the Carnot engine.
2) Calculate the work W produced per cycle and the heat Q_C rejected to the cold reservoir.
3) Calculate $\Delta S_{\mathrm{universe}}$ for one complete Carnot cycle. Interpret your result.
4) An irreversible engine operating between the same reservoirs and absorbing the same Q_H produces only $W' = 1200\,\mathrm{J}$ per cycle. Calculate the new Q'_C and the new $\Delta S_{\mathrm{universe}}$. What does this say about irreversible engines?

Exercise 13:

For any cyclic process, the **Clausius Inequality** states:

$$\oint \frac{\delta Q}{T} \leq 0$$

where equality holds for a reversible cycle.

1) Apply this inequality to a Carnot cycle (reversible) and verify that equality holds.
2) An engineer claims to have designed a heat engine operating between $T_H = 800\,\mathrm{K}$ and $T_C = 300\,\mathrm{K}$ that absorbs $Q_H = 10\,000\,\mathrm{J}$, produces $W = 6\,000\,\mathrm{J}$ of work, and rejects $Q_C = 4\,000\,\mathrm{J}$. Use the Clausius inequality to determine whether this engine is thermodynamically possible.
3) What is the maximum efficiency of any engine operating between these two temperatures?

Exercise 14:

A **refrigerator** operates between $T_C = 255\,\mathrm{K}$ (freezer compartment) and $T_H = 295\,\mathrm{K}$ (room temperature). It must remove $Q_C = 500\,\mathrm{J}$ per cycle from the freezer. Recall:

$$\mathrm{COP}_{\max} = \frac{T_C}{T_H - T_C}$$

1) Calculate the minimum work $W_{\min}$ required per cycle for a **reversible** (Carnot) refrigerator.

2) Calculate the Coefficient of Performance $\mathrm{COP} = Q_C/W$ for the reversible case.

3) Calculate $\Delta S_{\text{universe}}$ per cycle for the reversible refrigerator.

4) An actual refrigerator consumes $W = 120\,\mathrm{J}$ per cycle. Calculate its actual COP and $\Delta S_{\text{universe}}$. Is this device operating within the limits of the Second Law?