Thermodynamic Entropy and the Second Law

Class Notes

1 Thermodynamic Entropy

Last time, we derived that for a reversible Carnot cycle operating between a hot reservoir at T_H and a cold reservoir at T_C, the heats exchanged satisfy:

$$\frac{Q_H}{T_H} - \frac{Q_C}{T_C} = 0 \tag{1}$$

Recall that the efficiency of the Carnot engine is given by:

$$\eta_{\text{Carnot}} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H} \tag{2}$$

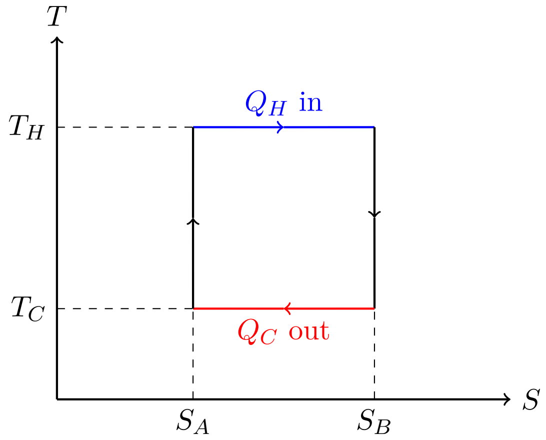
The quantity Q/T has units of Joules per Kelvin (J/K) in SI units. These are the units of **entropy**. We can define the entropy transferred during the heat exchange as:

$$S_H = \frac{Q_H}{T_H} \quad \text{(entropy entering the system)} \tag{3}$$

$$S_C = \frac{Q_C}{T_C} \quad \text{(entropy leaving the system)} \tag{4}$$

For a reversible Carnot process, $S_H = S_C$, meaning there is no net change to the entropy of the Universe ($\Delta S_{\text{univ}} = 0$).

We can visualize the Carnot process very simply in a Temperature-Entropy ($T - S$) diagram, where it forms a perfect rectangle:



2 General Reversible Processes

What about more general reversible processes? Any arbitrary reversible cycle in the $P - V$ plane can be broken down into a series of infinitesimal Carnot cycles. We accomplish this by drawing a grid of closely spaced **adiabatic lines** (where $S = \text{const}$) intersected by isothermal processes.

For each individual Carnot cycle operating between adjacent adiabats, the heat absorbed and expelled satisfies:

$$\frac{đQ_{\text{in}}}{T_{\text{in}}} = \frac{đQ_{\text{out}}}{T_{\text{out}}} \tag{5}$$

Summing over the entire arbitrary cycle, the internal boundaries cancel pairwise, and we are left with the boundary of the arbitrary process. This leads to the **Clausius Theorem** for a reversible cycle:

$$\oint \frac{đQ}{T} = 0 \tag{6}$$

This confirms that the entropy S, defined by $dS = đQ_{\text{rev}}/T$, is a true state function.

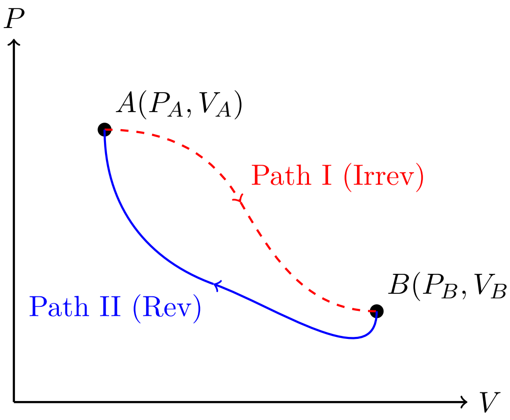
3 The Second Law and Irreversible Processes

For an irreversible cycle, the engine is less efficient than a Carnot engine, leading to the **Clausius Inequality**:

$$\oint \frac{đQ}{T} \leq 0 \tag{7}$$

Equality holds for reversible cycles, and the strict inequality holds for irreversible cycles. Is this the familiar Second Law of Thermodynamics? Let's verify.

Consider a system that undergoes a cyclic process consisting of an irreversible expansion from state A to state B (Path I), followed by a reversible compression from B back to A (Path II).



Applying the Clausius inequality to this full cycle:

$$\oint \frac{đQ}{T} \leq 0 \implies \int_{\text{Path I}} \frac{đQ}{T} + \int_{\text{Path II}} \frac{đQ}{T} \leq 0 \tag{8}$$

Because Path II is strictly reversible, the integral along this path is exactly the change in the state function S:

$$\int_{\text{Path II}} \frac{đQ_{\text{rev}}}{T} = S(A) - S(B) \tag{9}$$

Substituting this back into our inequality:

$$\int_{\text{Path I}} \frac{đQ}{T} + S(A) - S(B) \leq 0 \implies \int_{\text{Path I}} \frac{đQ}{T} \leq S(B) - S(A) \tag{10}$$

If Path I is **adiabatic** (meaning the system is isolated from the environment, so $đQ = 0$), then the integral vanishes, leaving:

$$0 \leq S(B) - S(A) \implies \boxed{S(B) \geq S(A)} \tag{11}$$

This is the familiar formulation of the Second Law: the entropy of an isolated system always increases (or remains constant if reversible). This monotonic increase is responsible for the **arrow of time**.

4 Reversible, Adiabatic, and Isentropic Processes

From our derivation above, we have the general rule for any infinitesimal process:

$$dS \geq \frac{đQ}{T} \tag{12}$$

For a completely reversible process, equality holds: $dS = \frac{đQ_{\mathrm{R}}}{T}$.

Let us clarify the distinctions between three commonly confused terms:

- **Reversible Adiabatic:** Since $đQ_R = 0$, it immediately follows that $dS = 0$. Therefore, a reversible adiabatic process is always **isentropic**.
- **Irreversible Adiabatic:** Since $đQ = 0$ but the process is irreversible, the strict inequality holds: $dS > 0$. Therefore, an irreversible adiabatic process is **not isentropic**.

What if a process is defined as **isentropic** ($dS = 0$)?

$$0 \geq \frac{đQ}{T} \implies đQ \leq 0 \tag{13}$$

There are two ways this can happen:

1. $đQ = 0$ (The process is reversible and adiabatic).
2. $đQ < 0$ (The process is irreversible, and heat is actively removed to offset the entropy generated by the irreversibility).

Summary:

- Reversible Isentropic $\implies$ Adiabatic ($đQ = 0$)
- Irreversible Isentropic $\implies$ Not Adiabatic ($đQ < 0$)

Conclusion: Isentropic ($dS = 0$), Adiabatic ($đQ = 0$), and Reversible are three distinct concepts that should not be used interchangeably.