Reversibility and the Second Law of Thermodynamics

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1 Review: The Zeroth and First Laws

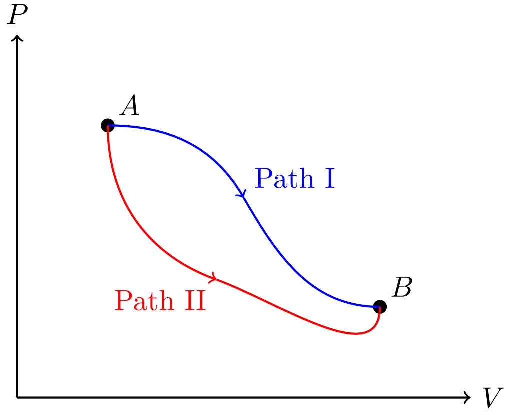
Last time, we saw the foundational laws of thermodynamics:

- **Zeroth Law:** Implies the existence of a function of state called the *temperature*, T.
- **First Law:** Implies the existence of a function of state called the internal *energy*, E.

The First Law is written in differential form as:

$$dE = đQ + đW \tag{1}$$

where $đQ$ is the heat added to the system and $đW$ is the work done on the system. For a gas, the work is given by $đW = -PdV$. Crucially, heat (Q) and work (W) are *not* functions of state.



Because E is a state function, the change in energy between two states is independent of the path taken:

$$\int_{\text{Any Path}} dE = E_B - E_A \tag{2}$$

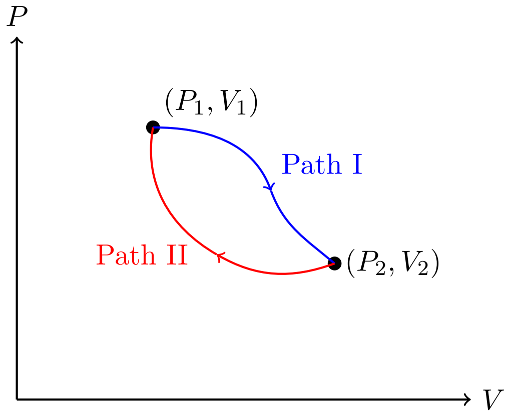
However, the work done (and thus the heat transferred) depends heavily on the path:

$$-\int_{\text{Path I}} PdV \neq -\int_{\text{Path II}} PdV \tag{3}$$

2 Reversible Processes and Cycles

Reversible processes are processes that can be run in both directions of time. They are a special, idealized case of quasi-static processes that can be run completely backward without dissipation.

Consider a "round trip" process (a thermodynamic cycle) as shown in the figure below: Start at (P_1, V_1), go to (P_2, V_2) via Path I, and then return to (P_1, V_1) via Path II.



By the First Law, over a complete closed cycle, the net change in internal energy is zero:

$$\oint dE = 0 \tag{4}$$

However, the total work done is clearly not zero ($\oint đW = -\oint PdV \neq 0$). The area enclosed by the loop represents the net work. To satisfy the First Law, this work must be balanced by the net heat absorbed by the system:

$$\oint đQ + \oint đW = 0 \implies \oint đQ = \oint PdV \tag{5}$$

Such a cycle can convert heat into macroscopic work (and vice versa). This is incredibly useful and forms the foundation of the **heat engine**, a concept fundamentally important to modern society.

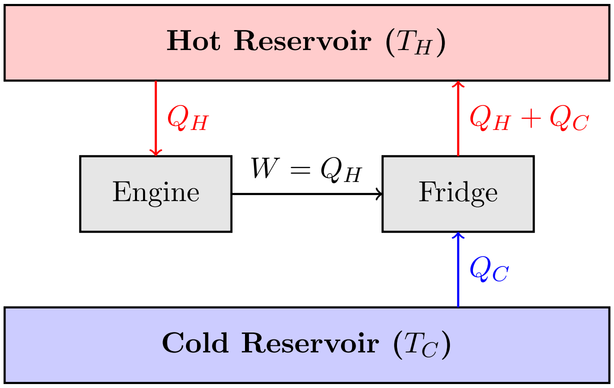
3 The Second Law of Thermodynamics

Although the First Law permits the conversion of heat into work, empirical evidence shows that there are strict limitations on how this conversion can occur. This leads us to the Second Law.

3.1 Kelvin and Clausius Statements

- **Kelvin's Statement:** "No process is possible whose sole effect is to extract heat from a reservoir and convert this entirely into work."
- **Clausius's Statement:** "No process is possible whose sole effect is the transfer of heat from a colder body to a hotter body." (i.e., you cannot build a refrigerator that works without an external energy input).

These two statements are logically equivalent. If you could violate Kelvin's statement (by building a perfect engine that converts heat Q_H directly into work W), you could use that work to power a standard refrigerator. The net effect of this combined system would be extracting heat from the cold reservoir and depositing it into the hot reservoir without any net external work—a direct violation of Clausius's statement.



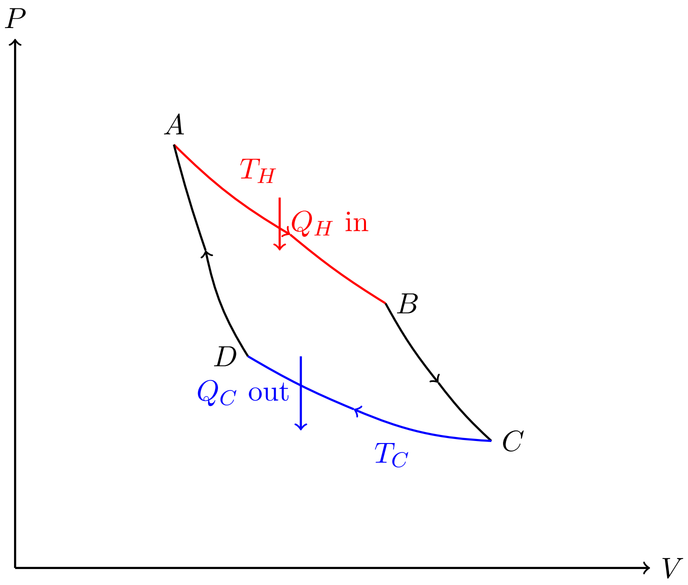
The combination violates Clausius's statement.

4 The Carnot Cycle

But wait a second, how is Kelvin's statement compatible with the physics of reversible cycles? We just saw that for a cycle, $\oint đQ = -\oint đW$. Is this a contradiction?

The key is that a reversible engine does more than just extract heat from a hot reservoir. It **must also deposit heat elsewhere!**

To see this, consider a particular kind of reversible cycle called the **Carnot Engine** (Sadi Carnot, 1824). The Carnot cycle operates entirely reversibly between two thermal reservoirs at temperatures T_H and T_C.



The four steps of the Carnot cycle are:

1. **A → B:** Isothermal expansion at $T = T_H$. The gas absorbs heat Q_H from the hot reservoir.
2. **B → C:** Adiabatic expansion to $T = T_C$. No heat is exchanged.
3. **C → D:** Isothermal contraction at $T = T_C$. The gas dumps heat Q_C into the cold surroundings.
4. **D → A:** Adiabatic contraction. The gas returns to T_H and the system is back to its exact original state.

Because the system returns to its initial state, the net change in energy over the cycle is zero ($\oint dE = 0$). Thus, the net work performed by the system must equal the net heat absorbed:

$$W = Q_H - Q_C \tag{6}$$

We define the **thermodynamic efficiency** (η_{carnot}) of the engine as the ratio of the useful work output to the heat input:

$$\boxed{\eta_{\text{carnot}} = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}} \tag{7}$$

Because $Q_C > 0$ strictly (to avoid violating Kelvin's statement), the efficiency can never reach 1 (100%). Some heat must always be dumped to a colder reservoir.