Physics 415 - Lecture 16: Heat Engines and Refrigerators

February 26, 2025

Summary

- First Law: $\Delta E = Q - W$. (Q=heat absorbed by system, W=work done by system). Differential form: $dE = \dbar Q - \dbar W$.
- Second Law: For an isolated system, total entropy change $\Delta S_{tot} \geq 0$.
  - $\Delta S_{tot} > 0$: Irreversible process.
  - $\Delta S_{tot} = 0$: Reversible process.
- Heat Bath/Reservoir: A very large system at temperature T. If it absorbs heat Q reversibly, its entropy changes by $\Delta S = Q/T$. Its temperature change $\Delta T = Q/C$ is negligible (assumed $C \to \infty$).

Heat Engines & Refrigerators

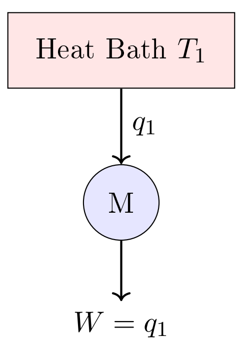
Heat Engine

A device (thermodynamic system) that operates in a cycle, absorbs heat, and converts part of this energy to work. In more detail:

- Device M (working substance) undergoes a cyclic process.
- In each cycle:
  - Heat q_1 is absorbed from a high-temperature reservoir (T_1).
  - Part of this energy is converted to work W.
  - Remaining heat q_2 is dumped to a lower-temperature reservoir ("heat sink") ($T_2 < T_1$).

The laws of thermodynamics ultimately limit the efficiency of such a heat engine.

A "Perfect" Heat Engine? Could an engine, in each cycle, convert *all* absorbed heat q_1 into work $W = q_1$, with $q_2 = 0$?



Such a device would not violate the First Law ($\Delta E_M = 0$ over cycle, $Q_{net} = q_1$, $W = q_1 \implies \Delta E_M = Q_{net} - W = 0$). However, the Second Law forbids such a machine. Let's analyze the total entropy change over one cycle:

$$\Delta S_{tot} = \Delta S_M + \Delta S_{heat\_bath}$$

Since M returns to its initial state after a cycle, $\Delta S_M = 0$. The heat bath loses heat q_1, so its entropy change is $\Delta S_{heat\_bath} = -q_1/T_1$.

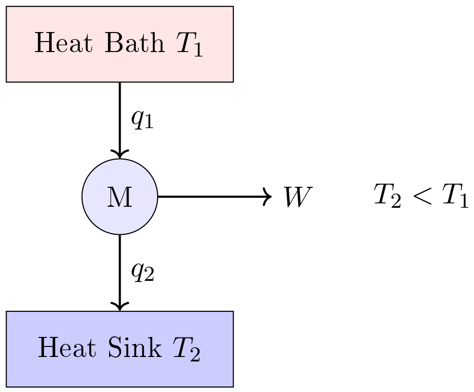
$$\implies \Delta S_{tot} = 0 + (-\frac{q_1}{T_1}) = -\frac{q_1}{T_1}$$

If the engine does positive work, $W = q_1 > 0$. Then $\Delta S_{tot} = -W/T_1 < 0$. This contradicts the Second Law ($\Delta S_{tot} \geq 0$). X (If $W \leq 0$, the process is allowed but useless as an engine).

Kelvin's Statement of the Second Law: "It is impossible to construct a perfect heat engine" (a device whose sole effect is to extract heat from a reservoir and convert it entirely into work).

From a statistical viewpoint: A perfect heat engine would require the spontaneous occurrence of a process in which some amount of energy, distributed randomly among the enormous number of degrees of freedom (DOF) of the bath, converts entirely into the ordered motion of a single DOF doing work (e.g., piston). This would correspond to a decrease in total entropy S, which is overwhelmingly improbable.

A "Real" Heat Engine (with two reservoirs): By introducing another heat bath at lower temperature T_2, where entropy increases, we can satisfy the Second Law:



Assume a cyclic process for M ($\Delta S_M = 0$). First Law: $\Delta E_M = (q_1 - q_2) - W = 0 \implies W = q_1 - q_2$. ($q_1, q_2, W$ are all positive quantities here). Second Law: $\Delta S_{tot} = \Delta S_1 + \Delta S_2 + \Delta S_M \geq 0$. $\Delta S_1 = -q_1/T_1$ (heat leaves reservoir 1). $\Delta S_2 = +q_2/T_2$ (heat enters reservoir 2).

$$\Delta S_{tot} = -\frac{q_1}{T_1} + \frac{q_2}{T_2} \geq 0$$

Substitute $q_2 = q_1 - W$:

$$-\frac{q_1}{T_1} + \frac{q_1 - W}{T_2} \geq 0$$

$$\frac{q_1}{T_2} - \frac{W}{T_2} \geq \frac{q_1}{T_1}$$

$$\frac{W}{T_2} \leq q_1 \left(\frac{1}{T_2} - \frac{1}{T_1}\right) = q_1 \frac{T_1 - T_2}{T_1 T_2}$$

$$W \leq q_1 \frac{T_1 - T_2}{T_1} = q_1 \left(1 - \frac{T_2}{T_1}\right)$$

This inequality limits the maximum work obtainable from heat q_1.

Define the "efficiency" η of the engine:

$$\eta = \frac{W}{q_1} = \frac{\text{what we get out (Work)}}{\text{what we put in (Heat } q_1)}$$

The Second Law implies:

$$\eta \leq 1 - \frac{T_2}{T_1}$$

An efficient engine requires $T_2 \ll T_1$ (large temperature difference: high T_1, low T_2).

The maximum possible efficiency is achieved for a reversible process, where $\Delta S_{tot} = 0$.

$$\eta_{max} = 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1}$$

This maximum efficiency is called the **Carnot Efficiency**. Roughly, a reversible engine avoids "friction" and processes that generate entropy, like heat transfer across large temperature differences.

Carnot Cycle

An example of a reversible cycle that achieves the maximum efficiency is the Carnot cycle. It consists of four reversible steps carried out on a working substance (e.g., gas, liquid):

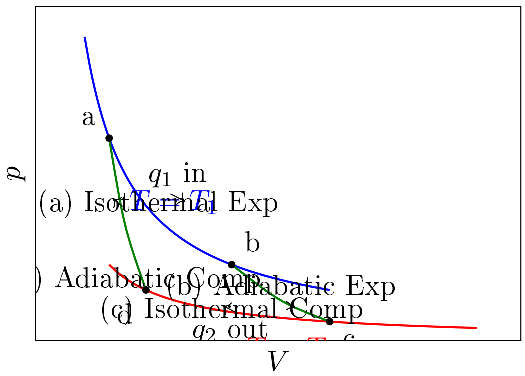
(a) Isothermal expansion at $T = T_1$. Heat q_1 absorbed from reservoir 1.

(b) Adiabatic expansion ($Q = 0$). Temperature drops from T_1 to T_2.

(c) Isothermal compression at $T = T_2$. Heat q_2 given off to reservoir 2.

(d) Adiabatic compression ($Q = 0$). Temperature rises from T_2 to T_1.

Carnot Cycle (p-V Diagram)



Since each stage is reversible, the total cycle is reversible, $\Delta S_{tot} = 0$, and the efficiency is $\eta = 1 - T_2/T_1 = \eta_{max}$. The working substance can be anything.

Example: Carnot Cycle with Ideal Gas Working substance = ν moles of ideal gas ($pV = \nu RT$, $E = \nu c_v T$).

- $a \to b$: Isothermal expansion at T_1. $\Delta E = 0$. $q_1 = W_{a\to b} = \int_{V_a}^{V_b} p dV = \int_{V_a}^{V_b} \frac{\nu R T_1}{V} dV = \nu R T_1 \ln(V_b/V_a)$.
- $b \to c$: Adiabatic expansion ($Q = 0$). $W_{b\to c} = -\Delta E = -\nu c_v (T_2 - T_1)$. Also $T_1 V_b^{\gamma-1} = T_2 V_c^{\gamma-1}$.

- $c \to d$: Isothermal compression at T_2. $\Delta E = 0$. $W_{c\to d} = \int_{V_c}^{V_d} p dV = \nu R T_2 \ln(V_d/V_c)$. Heat rejected $q_2 = -W_{c\to d} = \nu R T_2 \ln(V_c/V_d)$.
- $d \to a$: Adiabatic compression ($Q = 0$). $W_{d\to a} = -\Delta E = -\nu c_v(T_1 - T_2)$. Also $T_2 V_d^{\gamma-1} = T_1 V_a^{\gamma-1}$.

Total work done by gas:

$$W = W_{a\to b} + W_{b\to c} + W_{c\to d} + W_{d\to a}$$

$$W = \nu R T_1 \ln(V_b/V_a) - \nu c_v(T_2 - T_1) + \nu R T_2 \ln(V_d/V_c) - \nu c_v(T_1 - T_2)$$

The c_v terms cancel.

$$W = \nu R T_1 \ln(V_b/V_a) + \nu R T_2 \ln(V_d/V_c)$$

From adiabatic steps: $T_1 V_b^{\gamma-1} = T_2 V_c^{\gamma-1}$ and $T_1 V_a^{\gamma-1} = T_2 V_d^{\gamma-1}$. Dividing these equations: $(V_b/V_a)^{\gamma-1} = (V_c/V_d)^{\gamma-1} \implies V_b/V_a = V_c/V_d$. Let $r = V_b/V_a$. Then $V_d/V_c = V_a/V_b = 1/r$. $\ln(V_d/V_c) = \ln(1/r) = -\ln r$.

$$W = \nu R T_1 \ln r - \nu R T_2 \ln r = \nu R(T_1 - T_2) \ln r$$

Efficiency:

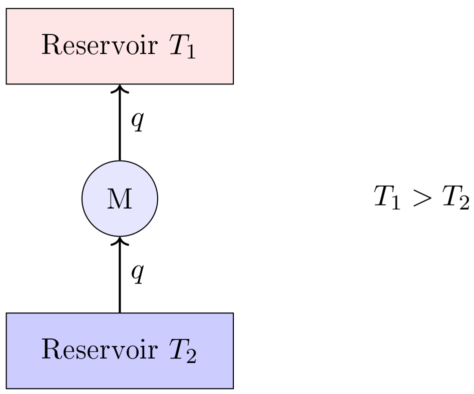
$$\eta = \frac{W}{q_1} = \frac{\nu R(T_1 - T_2)\ln r}{\nu R T_1 \ln r} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

This confirms the Carnot efficiency for the ideal gas example. ✓

Refrigerator

A device, operating in a cycle, that removes heat q_2 from a low-temperature reservoir (T_2) and rejects heat q_1 to a higher-temperature reservoir (T_1). This requires work input W. Essentially a heat engine run in reverse.

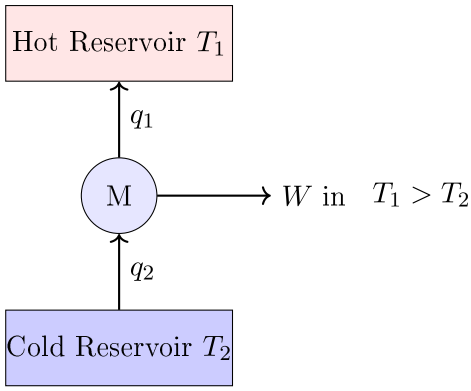
A "Perfect" Refrigerator? Could heat q flow spontaneously from cold T_2 to hot T_1 without work input ($W = 0$)?



This violates the Second Law. Over one cycle ($\Delta S_M = 0$): $\Delta S_{tot} = \Delta S_1 + \Delta S_2 = \frac{q}{T_1} - \frac{q}{T_2} = q\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$. Since $T_1 > T_2$, $(1/T_1 - 1/T_2) < 0$. If $q > 0$, then $\Delta S_{tot} < 0$. X

Clausius Statement of the Second Law: "It is impossible to construct a perfect refrigerator" (a device whose sole effect is to transfer heat from a colder body to a hotter body).

A "Real" Refrigerator: Requires work input W.



First Law (over cycle): $\Delta E_M = Q_{net} - W_{net} = (q_2 - q_1) - (-W) = 0 \implies q_1 = q_2 + W$. (Heat rejected = heat absorbed + work input). Second Law: $\Delta S_{tot} = \Delta S_1 + \Delta S_2 \geq 0 \implies \frac{q_1}{T_1} - \frac{q_2}{T_2} \geq 0$.

$$\frac{q_2 + W}{T_1} \geq \frac{q_2}{T_2} \implies \frac{W}{T_1} \geq q_2 \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = q_2 \frac{T_1 - T_2}{T_1 T_2}$$

$$W \geq q_2 \frac{T_1 - T_2}{T_2}$$

The "Coefficient of Performance" (COP) K for a refrigerator is:

$$K = \frac{q_2}{W} = \frac{\text{what we want (Heat extracted from cold)}}{\text{what we pay for (Work input)}}$$

From the Second Law inequality:

$$K \leq \frac{T_2}{T_1 - T_2}$$

The maximum COP is $K_{max} = \frac{T_2}{T_1 - T_2}$, achieved by a reversible refrigerator (e.g., reversed Carnot cycle).