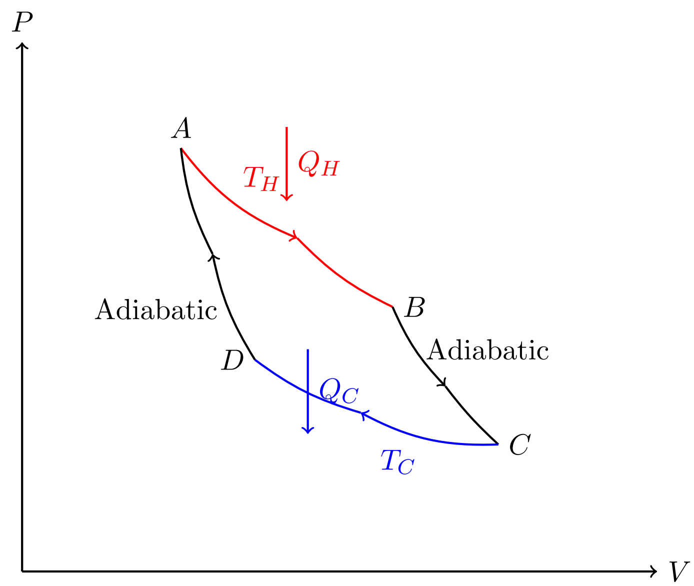
Carnot's Theorem and the Second Law

PHYS 301; Prof. Cyr-Racine

1 The Reversible Carnot Cycle

Last time, we introduced the reversible Carnot cycle. Because it is completely reversible, there is no friction or dissipation of energy. The cycle operates between a hot reservoir at temperature T_H and a cold reservoir at temperature T_C, and can be visualized on a Pressure-Volume ($P - V$) diagram:



The thermodynamic efficiency (η) of the engine is defined as the ratio of the net work done (W) to the heat absorbed from the hot reservoir (Q_H):

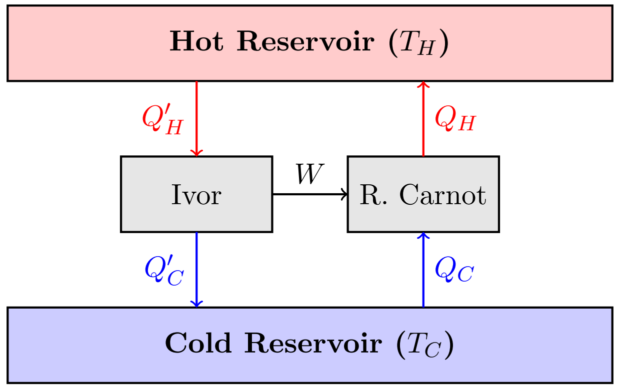
$$\eta_{\text{Carnot}} \equiv \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} \tag{1}$$

From Kelvin's statement of the Second Law of Thermodynamics, we know that heat cannot be perfectly converted into work without dumping some heat to a cold reservoir. Therefore, we must have $Q_C > 0$, which implies that $\eta_{\text{Carnot}} < 1$.

2 Carnot's Theorem

Carnot's Theorem: The Carnot engine is the most efficient engine possible operating between two thermal reservoirs at temperatures T_H and T_C.

To prove this, let us assume we have an arbitrary (potentially irreversible) engine, which we will call "Ivor", operating alongside a reversible Carnot engine ("R. Carnot"). We run the reversible Carnot engine in reverse as a refrigerator, driven entirely by the work output W of Ivor.



For the combined system of the two engines:

- Net heat absorbed from the hot reservoir: $Q'_H - Q_H$
- Net heat dumped to the cold reservoir: $Q'_C - Q_C$

Because the two engines are coupled such that the work output of Ivor exactly powers the Carnot refrigerator, the combined system does zero net external work. Therefore, by the First Law of Thermodynamics (conservation of energy), the net heat absorbed must equal the net heat dumped:

$$Q'_H - Q_H = Q'_C - Q_C \tag{2}$$

We can also derive this by considering the energy balance of the engines separately:

$$\text{Ivor (Engine):} \quad Q'_H = W + Q'_C \implies W = Q'_H - Q'_C \tag{3}$$
$$\text{R. Carnot (Fridge):} \quad Q_C + W = Q_H \implies W = Q_H - Q_C \tag{4}$$

Equating the work W for both:

$$\begin{aligned} Q'_H - Q'_C &= Q_H - Q_C \\ \implies Q'_H - Q_H &= Q'_C - Q_C \end{aligned} \tag{5}$$

According to **Clausius's statement** of the Second Law, heat cannot spontaneously flow from a cold body to a hot body without external work. Since our combined system requires zero net external work, it cannot transfer a net amount of heat into the hot reservoir. Therefore, the net heat absorbed from the hot reservoir must be positive or zero:

$$Q'_H - Q_H \geq 0 \implies Q'_H \geq Q_H \tag{6}$$

Now, let us compute the efficiency of the irreversible engine Ivor (η_{Ivor}). Using the definition of efficiency and substituting $Q'_C = Q'_H - Q_H + Q_C$ from Equation (5):

$$\begin{aligned}
\eta_{\text{Ivor}} &= 1 - \frac{Q'_C}{Q'_H} \\
&= 1 - \frac{Q'_H - Q_H + Q_C}{Q'_H} \\
&= \frac{Q'_H - (Q'_H - Q_H + Q_C)}{Q'_H} \\
&= \frac{Q_H - Q_C}{Q'_H}
\end{aligned} \tag{7}$$

Since $Q'_H \geq Q_H$, dividing by a larger denominator makes the fraction smaller (or equal). Therefore:

$$\eta_{\text{Ivor}} = \frac{Q_H - Q_C}{Q'_H} \leq \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} = \eta_{\text{Carnot}} \tag{8}$$

Thus, $\boxed{\eta_{\text{Ivor}} \leq \eta_{\text{Carnot}}}$.

Equality holds ($\eta_{\text{Ivor}} = \eta_{\text{Carnot}}$) if and only if $Q'_H = Q_H$ and $Q'_C = Q_C$. This perfect balance only happens if the engine Ivor is itself completely reversible.

3 Thermodynamic Temperature Definition

In classical thermodynamics, the absolute temperature scale is defined in terms of the efficiency of the reversible Carnot cycle. We define the temperatures T_H and T_C macroscopically such that:

$$\eta_{\text{Carnot}} = 1 - \frac{Q_C}{Q_H} \equiv 1 - \frac{T_C}{T_H} \tag{9}$$

This is in contrast to statistical mechanics, where temperature is fundamentally defined microscopically via entropy S and internal energy E:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} \tag{10}$$