Carnot Cycles and Second Law

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1 Statements of the Second Law of Thermodynamics

These are two equivalent statements of the second law of thermodynamics.

> **Kelvin-Planck Statement**: No system can absorb heat from a single reservoir and convert it entirely into work without additional net changes in the system or its surroundings.
>
> **Clausius Statement**: A process whose only net result is to absorb heat from a cold reservoir and release the same amount of heat to a hot reservoir is impossible.

We can show that the Kelvin-Planck and Clausius statements are equivalent by proving that, if either of these postulates is false, the other is also false. In particular, let us first assume that the Kelvin-Planck statement is false. Then we could perform a transformation whose sole result is to transform a definite amount of heat from a source at temperature T_1 to work. By means of friction, we could convert this work back to heat, thus raising the temperature of another body regardless of the value of its initial temperature T_2. If we let $T_2 > T_1$, the result of this transformation would be the transfer of heat from a cold reservoir to a hot reservoir without any loss, in violation of the Clausius statement. To show that the Kelvin-Planck statement must be false when the Clausius statement is false, we must discuss heat engines, particularly the Carnot cycle.

2 The Carnot Cycle

The Carnot cycle is the particular heat engine shown in figure 1. It consists of four reversible steps:

1. Isothermal absorption of heat from a hot reservoir,
2. Adiabatic expansion to a lower temperature,
3. Isothermal release of heat into a cold reservoir,
4. Adiabatic compression to the original state.

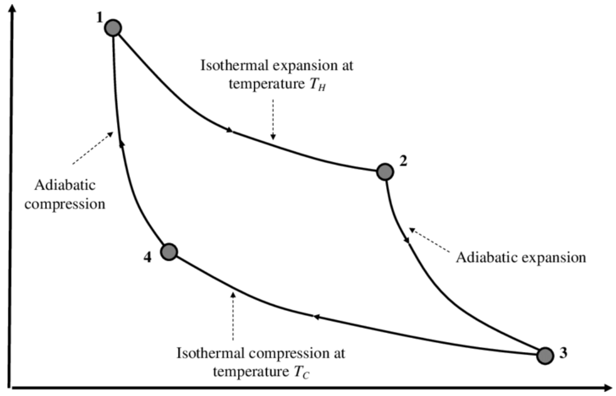
By the first law, the work done by this heat engine on its surroundings is equal to the net heat gained by the system. Let Q_H be the heat gained during step 1 and Q_C be the heat released in step 4. Then the work done is $Q_H - Q_C$, and the efficiency is

$$\eta = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}.$$

We can calculate Q_H as

$$Q_H = W_{\text{by gas}} = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \frac{nRT_H}{V} dV = nRT_H \ln\left(\frac{V_2}{V_1}\right).$$

Figure 1: Carnot Cycle



Similarly, we have

$$Q_C = W_{\text{on gas}} = nRT_C \ln\left(\frac{V_3}{V_4}\right).$$

From the rule we derived early for adiabatic processes, we have

$$T_H V_2^{K-1} = T_C V_3^{K-1},$$
$$T_H V_1^{K-1} = T_C V_4^{K-1},$$

so

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}.$$

Thus, the heat ratio is

$$\frac{Q_C}{Q_H} = \frac{T_C}{T_H},$$

so the efficiency is

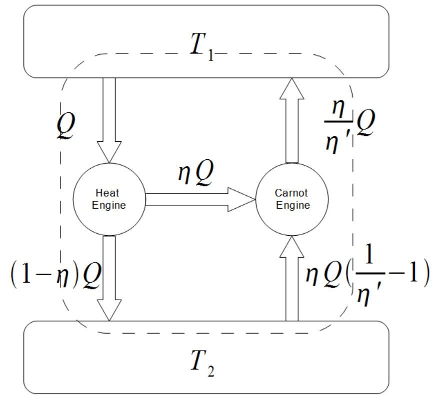
$$\eta = 1 - \frac{T_C}{T_H}. \tag{1}$$

We can now prove that the Kelvin-Planck statement must be false when the Clausius statement is false. Assume that we can transfer heat Q_H from the reservoir at T_C to T_H with no other effects. We can then run the Carnot cycle and deliver heat Q_C to the reservoir at T_C and perform some work. The end result is that there was no net heat change at the reservoir at T_H, the reservoir at T_C had some heat loss, and work was performed. This violates the Kelvin-Planck statement, as we have extracted heat from the reservoir at T_C and converted it to work without any other effects.

3 Carnot's Theorem

It turns out the Carnot cycle has the maximum possible efficiency of any heat engine. To prove this, consider the system in figure 2, where η is the efficiency of the heat engine and η' is the efficiency of the Carnot engine. The Carnot engine is run in reverse, as shown, and $T_1 > T_2$. If we have $\eta > \eta'$, the result is that heat is transferred from a cold reservoir to a hot one with no side effects. This directly violates the Clausius statement of the second law.

Figure 2: System for Carnot's Theorem Proof



4 Entropy

For our Carnot engine, we have

$$\frac{Q_H}{T_H} = \frac{Q_C}{T_C}.$$

This means that the path integral of $\frac{\Delta Q}{T}$ is zero around our cycle. Based on this, we define the *entropy* S by the equation

$$\Delta S = \frac{\Delta Q}{T}.$$

Then $\Delta S = 0$ for the Carnot cycle (or any reversible transformation) and $\Delta S \geq 0$ in general.

5 Problems

1. Suppose that two heat engines are connected in series, such that the heat released by the first engine is used as the heat absorbed by the second engine. The efficiencies of the engines are η_1 and η_2, respectively. Show that the net efficiency of the combination is given by $\eta_{\text{net}} = \eta_1 + \eta_2 - \eta_1\eta_2$.
2. Consider two objects with equal heat capacities C and initial temperatures T_1 and T_2. A Carnot engine is run using these objects as its hot and cold reservoirs until they are at equal temperatures. Assume that the temperature changes of both the hot and cold reservoirs is very small compared to the temperature during any one cycle of the Carnot engine.

   a) Find the final temperature T_f of the two objects, and the total work W done by the engine.
   Now consider three objects with equal and constant heat capacity at initial temperatures $T_1 = 100$ K, $T_2 = 300$ K, and $T_3 = 300$ K. Suppose we wish to raise the temperature of the third object. To do this, we could run a Carnot engine between the first and second objects, extracting work W. This work can then be dissipated as heat to raise the temperature of the third object. Even better, it can be stored and used to run a Carnot engine between the first and third object in reverse, which pumps heat into the third object. Assume that all work produced by running engines can be stored and used without dissipation.

   b) Find the minimum temperature T_L to which the first object can be lowered.

   c) Find the maximum temperature T_H to which the third object can be raised.