Second Law of Thermodynamics

First law of Thermodynamics has taught us, that we cannot get work without a supply of energy (for example, burning of fuel) and spending some energy, we can get only an equivalent amount of work, not more. Second law of Thermodynamics imposes some further restriction. Even after extracting heat from a heat source, we cannot get an equivalent amount of work. A fraction of the heat energy extracted has to be deposited to a so-called 'heat sink' and the remaining part may be converted to work.

Kelvin - Planck Statement of 2nd law : It is impossible for a machine, **working in a cycle**, to extract heat from a single source and convert it **fully** to work.

Clausius Statement of 2nd law : It is impossible for a machine to transport heat from a low temperature body to a high temperature body, **without the aid of external work**.

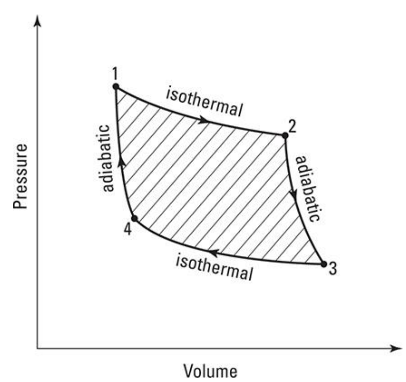
Although sounds completely different, it can be proved by pure logic, that the two versions of second law are actually equivalent.

A machine which converts heat energy to work, is called a **heat engine**. It works between two heat reservoirs, and in accordance with the Kelvin – Planck statement, it extracts say Q_1 amount of heat from the reservoir at higher temperature, deposits Q_2 amount of it to the reservoir at lower temperature and the converts the remaining amount : $(Q_1 - Q_2)$ to work.

Thermal efficiency (η) of an engine is defined as the ratio of the work (W) produced to the amount of heat (Q_1) extracted from the 'source'.

$\eta =$ $\mathbf{W/Q_1}$ (expressed as a ratio), or $\mathbf{W/Q_1 \times 100}$ (expressed as a percentage)

Carnot Engine



Carnot's engine is an ideal heat engine, which consists of a cylinder fitted with a piston that slides **without friction** and filled with **an ideal gas**. The walls of the cylinder and the piston is **completely non-conducting**, while its flat base is **perfectly conducting**. Clearly (because of the restrictions written in bold face), such an engine is not realizable in reality. It works in a cycle with four steps. The steps are shown in the indicator diagram.

Isothermal Expansion : The cylinder is placed on an **infinite** heat source at absolute temperature = T_1. The gas remains in equilibrium with the source and expands isothermally from (P_1, V_1) to (P_2, V_2). The work done : $W_1 = \int P\, dV$.

$$PV = nRT_1 \Rightarrow P = nRT_1/V \Rightarrow \mathbf{W_1 = nRT_1 \int dV/V = nRT_1 \ln (V_2/V_1)}$$

The internal energy of the gas does not change, because, the internal energy of an ideal gas depends only on temperature and remains unaltered as long as temperature doesn't change.

So, $\mathbf{\Delta U_1 = 0}$

The energy for performing the external work comes from the heat source.

Since, $\Delta U_1 = 0$, the heat extracted from the source : $\mathbf{Q_1 = W_1 = nRT_1 \ln (V_2/V_1)}$

Adiabatic Expansion : The cylinder is now placed on an insulating surface. The gas expands adiabatically from (P_2, V_2) to (P_3, V_3). As no heat comes from outside, the gas performs work at the cost of its own internal energy and hence cools down to T_2.

Work done : $\mathbf{W_2 = nC_v (T_1 - T_2)}$.

Isothermal Compression : Next, the cylinder is placed on an **infinite** heat source at absolute temperature = T_2, called the 'sink'. The gas is compressed isothermally from (P_3, V_3) to (P_4, V_4).

The work done : $W_3 = \mathbf{nRT_2 \ln (V_4/V_3) = - nRT_2 \ln (V_3/V_4)}$.

Note that the W_3 is –ve (as $V_3 > V_4$) $\Rightarrow$ work is done 'on the gas' not 'by the gas'.

Since $\Delta U_3 = 0$, again, the heat deposited to the sink :

$\mathbf{Q_2 = W_3 = nRT_2 \ln (V_3/V_4)}$

Adiabatic Compression : Finally, the cylinder is placed again on an insulating surface. The gas is compressed adiabatically from (P_4, V_4) to (P_1, V_1). It gets heated up From the temperature T_2 to T_1 and the work done in the process :

$\mathbf{W_4 = nC_v (T_2 - T_1)}$,

The total work done in the cycle W thus equals : $W_1 + W_2 + W_3 + W_4 = W_1 + W_3$ (as W_2 and W_4 cancels each other).

Now, since the points B and C are on an adiabatic curve : $T_1 V_2^{\gamma - 1} = T_2 V_3^{\gamma - 1}$

Similarly, as A and D are on an adiabatic curve : $T_1 V_1^{\gamma - 1} = T_2 V_4^{\gamma - 1}$

$\Rightarrow (V_2 / V_1)^{\gamma - 1} = (V_3 / V_4)^{\gamma - 1}$

$\Rightarrow \ln (V_2/V_1) = \ln (V_3/V_4)$.

$$\begin{aligned} \Rightarrow W &= nRT_1 \ln (V_2/V_1) - nRT_2 \ln (V_3/V_4) \\ &= nRT_1 \ln (V_2/V_1) - nRT_2 \ln (V_2/V_1) \\ &= nR (T_1 - T_2) \ln (V_2/V_1) \end{aligned}$$

and $Q_1 = nRT_1 \ln (V_2/V_1)$.

Therefore, efficiency $\boldsymbol{\eta = (T_1 - T_2)/T_1 = (1 - T_2/T_1)}$.

The more T_1 is increased and T_2 is decreased, the more efficient the engine becomes and as $\mathbf{T_1 \to T_2,\ \eta \to 0}$.

Entropy

You may note that though the above process is cyclic, the total work done $W \neq 0$, neither is the total heat exchange ($Q_1 - Q_2$). This is a reflection of the fact that dW and dQ are not exact differentials. In other words, their integrals around a closed loop, do not vanish. However, for Carnot cycle,

$$Q_1/T_1 - Q_2/T_2 = nR \ln (V_2/V_1) - nR \ln (V_2/V_1) = 0.$$

If we define : $\mathbf{dS = dQ/T}$, then the total change in the quantity 'S' = $\int dQ/T = 0$, around the closed loop, showing that dS is an 'exact differential'. We call 'S' as '**Entropy**' (dS is a small change in entropy).

This is an abstract definition. Later on, we shall see, that physically, entropy measures the '**disorder**' within a system.