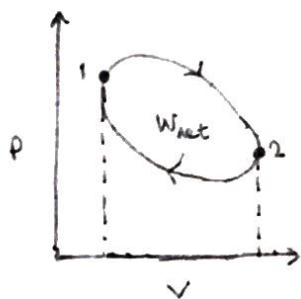


Heat Engines

A heat engine is a machine that converts Heat into useful work. It is historically one of the greatest inventions of mankind.

To be honest, converting heat into work is not that hard. Consider the isothermal expansion of an ideal gas. Since $dT = 0$, we know $dU = 0$ so $dQ = -dW$. However, this does not qualify as a heat engine since, to be useful, an engine has to generate work in a sustained fashion. The volume or pressure in isothermal expansion can't increase infinitely, so an engine like that would be useless. We need to use a thermodynamic cycle, thermodynamic processes defined in a closed loop.

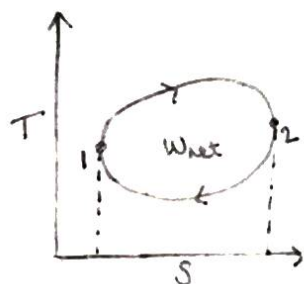
The loop will look something like:



The net work of the engine is given by the area of the loop. This can be worked out by subtracting the work done on the engine by the environment from the work done by the engine on the environment.

$$W_{\text{net}} = W_{1 \rightarrow 2} - W_{2 \rightarrow 1} = \int_1^2 P dV - \int_2^1 P dV = \oint P dV$$

Since $\oint dU = 0$ (the change in internal energy of a closed loop is always 0), $\oint dQ = \oint P dV = W_{\text{net}}$. $W_{\text{net}} = Q_H - Q_L$



From $W_{\text{net}} = \oint dQ$, we can say that for T-S plane:

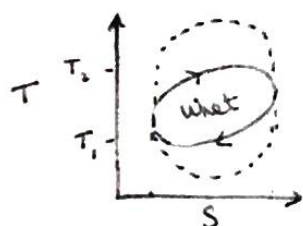
$$W_{\text{net}} = \int_1^2 T dS - \int_2^1 T dS = \oint T dS$$

Efficiency

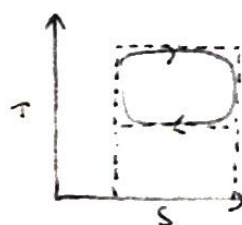
The intuitive definition of efficiency is $\eta = \frac{\text{desired output}}{\text{required input}}$

$$\therefore \eta = \frac{W_{\text{net}}}{Q_H} \quad \text{but } W_{\text{net}} = Q_H - Q_L \Rightarrow \eta = \frac{Q_H - Q_L}{Q_H}$$

$$\therefore \boxed{\eta = 1 - \frac{Q_L}{Q_H}} \quad \text{This is always true. So now can we go about maximising this?}$$



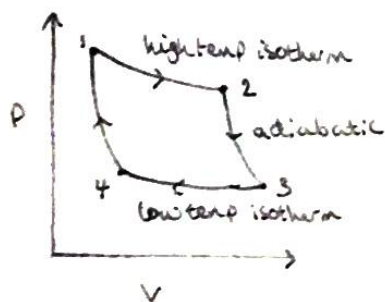
We need to find ways of maximising the area in the closed loop. One clear way of doing this is to increase the temperature difference, as shown on the left.



Another way is to make the loop less round. This maximises the area. This can be done by using isothermal expansion/compression, and adiabatic processes.

Doing all this points us towards a maximum efficiency for an engine, described by a cycle with perfect isothermal and adiabatic processes. This ideal cycle is called the Carnot Cycle.

This cycle can also be shown on a P-V diagram:



$$W_{1 \rightarrow 2} = - \int_{V_1}^{V_2} P dV = - n_m R T_H \ln\left(\frac{V_2}{V_1}\right) = - T_H dS$$

$$W_{2 \rightarrow 3} = \Delta U_{2 \rightarrow 3} = C_V (T_L - T_H)$$

$$W_{3 \rightarrow 4} = \int_{V_3}^{V_4} P dV = n_m R T_L \ln\left(\frac{V_4}{V_3}\right) = T_L dS$$

$$W_{4 \rightarrow 1} = \Delta U_{4 \rightarrow 1} = C_V (T_H - T_L)$$

$$\text{Net work} = \oint P dV = - (W_{12} + W_{23} + W_{34} + W_{41}) = \Delta S (T_H - T_L)$$

The efficiency is given by $\eta = \frac{W_{\text{net}}}{Q_H} = \frac{\Delta S(T_H - T_L)}{\Delta S T_H}$

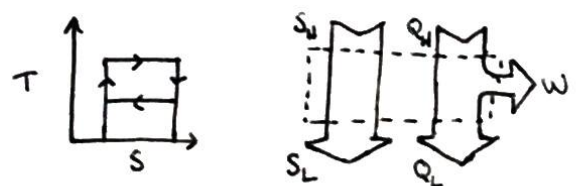
$$\eta_{\text{Carnot}} = 1 - \frac{T_L}{T_H}$$

This is the maximum possible efficiency of a heat engine, called the Carnot Efficiency.

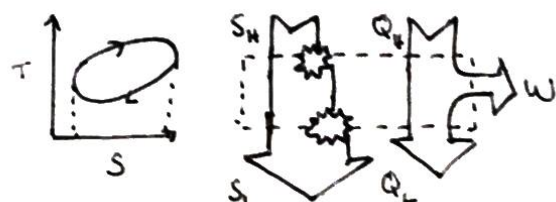
An ideal engine operating with this efficiency is called a Carnot Engine. An engine like that would also be reversible only if heat is exchanged just between the high temperature and low temperature reservoir and not with the environment. Otherwise, the total entropy increases. The cycle would also have to be traced infinitely close to equilibrium, which would take an infinite amount of time.

For these reasons, a Carnot engine is not only practically unachievable, it is also practically useless.

Entropy flow is also different between a Carnot Engine and a real engine:



T-S Plot and entropy diagram for Carnot Engine



T-S Plot and entropy diagram for Real Engine

As can be seen, there are increases in the entropy in the real engine. This has been introduced by mechanisms like friction. The output work in the real engine will also be smaller than the Carnot engine.

Refrigerators and Heat Pumps

With heat engines, more heat enters the engine than leaves it. The difference in heat becomes work on the environment. By tracing the same loop in the opposite direction, we can make a refrigerator or a heat pump. The difference between the two is one of purpose: a refrigerator draws heat away from an already cold reservoir, whereas a heat pump adds heat to an already hot reservoir. Work has to be done on the system since the heat flow is in the opposite direction to what would happen naturally.

We can define an efficiency for heat pumps and refrigerators, called a coefficient of performance. There is an associated Carnot coefficient as well.

for refrigerators:

$$K = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L}$$

$$K_{\text{Carnot}} = \frac{T_L}{T_H - T_L}$$

for Heat Pumps:

$$K = \frac{Q_H}{W} = \frac{Q_H}{Q_H - Q_L}$$

$$K_{\text{Carnot}} = \frac{T_H}{T_H - T_L}$$

Early Formulations of the Second Law

Early formulations of the second law were made prior to the understanding of entropy and were thus made with reference to heat.

Kelvin's Formulation: No process is possible whose sole result is the complete conversion of heat into work.

Clausius' Formulation: No process is possible whose sole result is the transfer of heat from a colder to a hotter body.

It is clear that if these two are violated, then the total entropy would decrease, violating our modern understanding of the second law.