Second Law of Thermodynamics

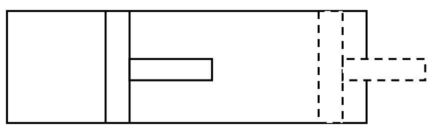
As an introduction to the Second Law of Thermodynamics, recall the First Law. The First Law is a statement of conservation of energy expressed for a process as:

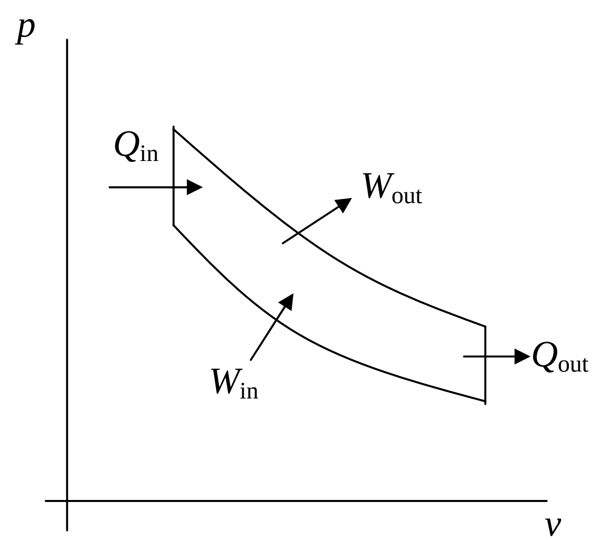
$$\Delta U = Q_{12} - W_{12}$$

and for a cycle as:

$$\sum Q = \sum W$$

Consider some limitations of the First Law. Take a piston-cylinder example such as the spark ignition (Otto cycle) automotive cycle.





There are four processes in this cycle:

- Compression of the gas
- Heat addition via the chemical reaction
- Expansion of the gas
- Heat rejection (expelling the gas from the cylinder)

For the cycle we have:

$$\sum Q = Q_{in} - Q_{out} = \sum W = -W_{in} + W_{out} = W_{net}$$

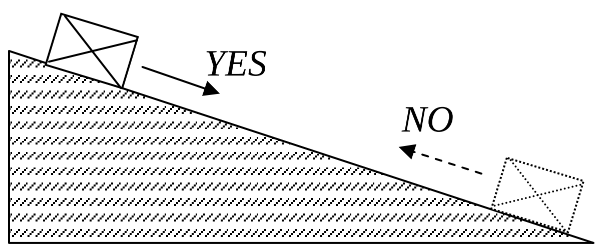
The efficiency of the energy conversion, from Q_{in} to W_{net} is given as

$$\eta = \frac{W_{net}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

From the expression for the efficiency there is no indication to the limits on the relative values of Q's. For example, Q_{out} could be as small as we please without violating the energy balance and thus approach a 100% efficiency of conversion from heat to work. Thus the First law does not limit the extent of the conversion of one form of energy to another.

The first law also does not indicate if a particular process or cycle is feasible as long as it does not violate the first law.

The first law does not indicate the direction of a process. For example, a block left on an inclined plane will spontaneously slide down (in a gravitational field and with negligible friction). However a block at the bottom of the inclined plane will not spontaneously move up.



Aspects of the Second Law.

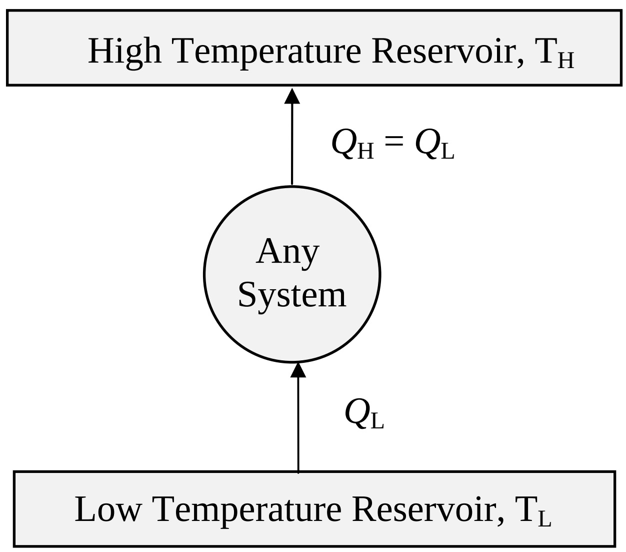
The second law of thermodynamics and deductions from it will provide a means for

- Predicting the direction of processes
- Establishing conditions of equilibrium
- Determining the best theoretical performance of cycles, engines, and other devices
- Defining a temperature scale independent of the properties of thermodynamic substance

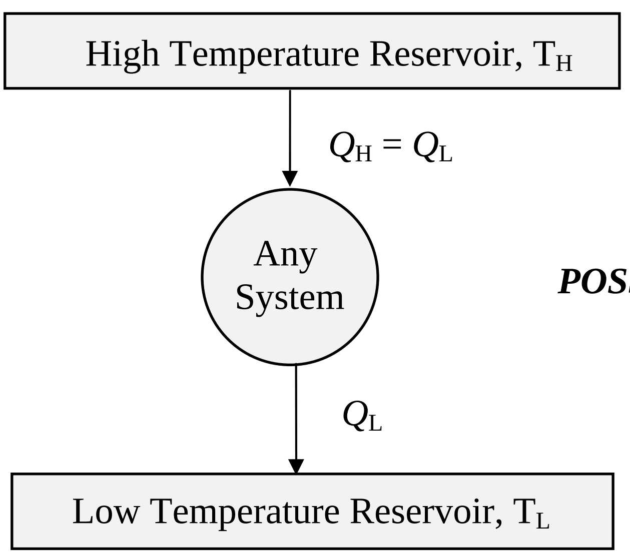
Statements of the Second Law of Thermodynamics

<u>Clausius Statement:</u> Application: Refrigerators and Heat Pumps

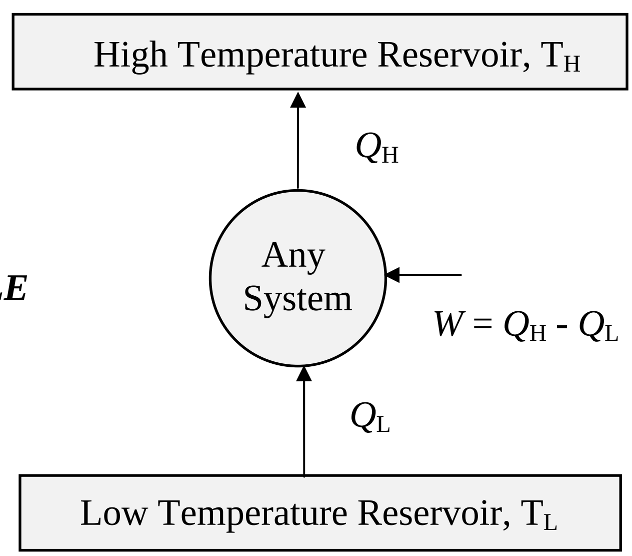
It is impossible for any system to operate in such a way that the sole result would be an energy transfer by heat from a cooler to a hotter body.



NOT POSSIBLE

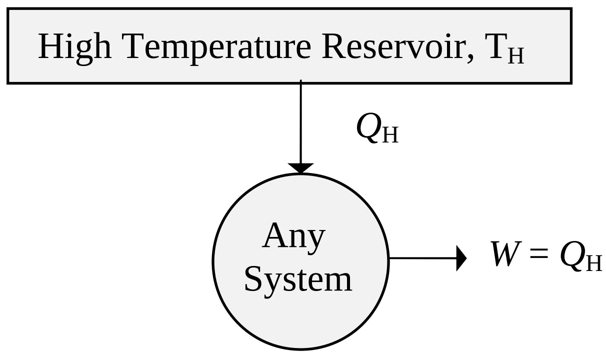


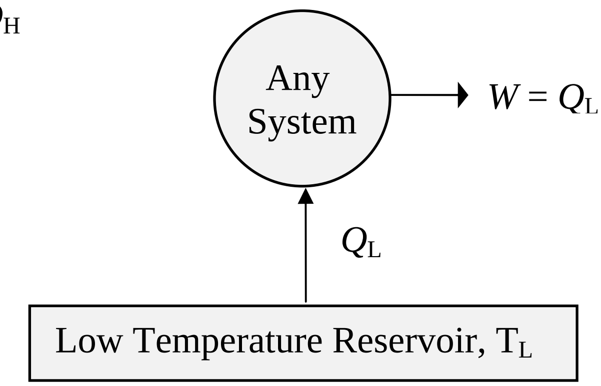
POSSIBLE



Kelvin-Plank Statement - Application: Heat Engines

It is impossible for any system to operate in a thermodynamic cycle and deliver a net amount of work to its surroundings while receiving energy by heat transfer from a single thermal reservoir.





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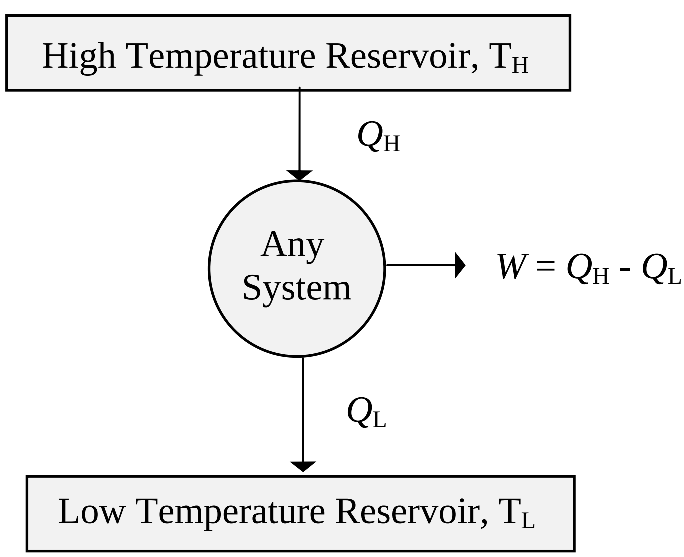


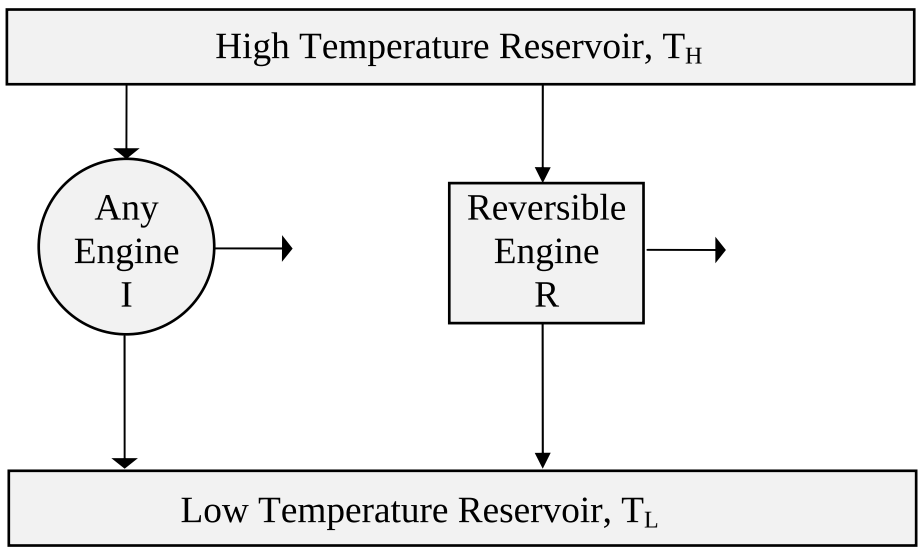
POSSIBLE

The Clausius and the Kelvin-Plank statements are equivalent.

The equivalence is demonstrated by showing that the violation of one statement implies the violation of the other.

Second Law Corollaries

It is impossible to construct an engine, operating between two given thermal reservoirs, that is more efficient than a reversible engine operating between the same two reservoirs.



Proof:

1) Let any heat engine I and a reversible engine R operate between the high and low temperature reservoirs T_H and T_L.

2) Assume the statement above is false, i.e. assume

$$\eta_I > \eta_R$$

3) Operate the engines such that

$$Q_{IH} = Q_{RH} = Q_H$$

4) By definition:

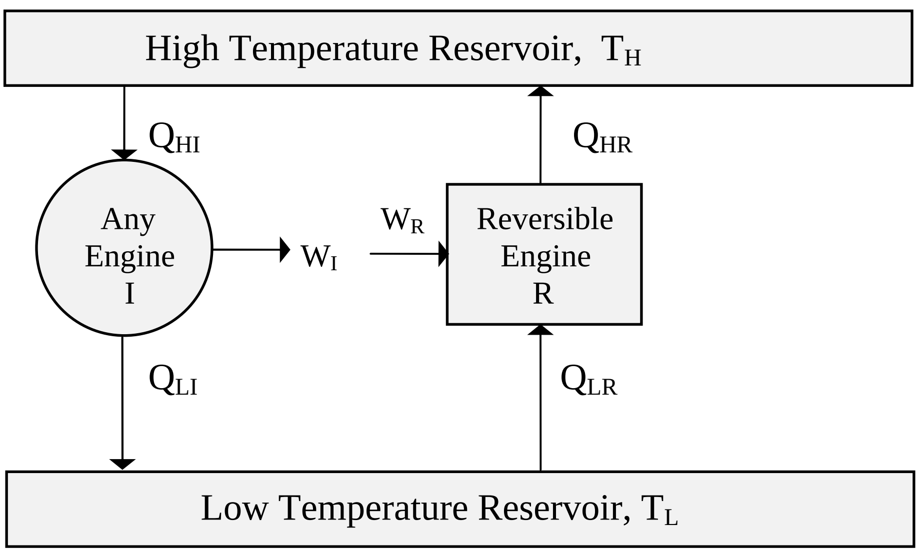
$$\eta = \frac{Wnet}{Qin} \quad \text{and} \quad \eta_I = \frac{WI}{QH}, \quad \eta_R = \frac{WR}{QH}$$

by assumption:

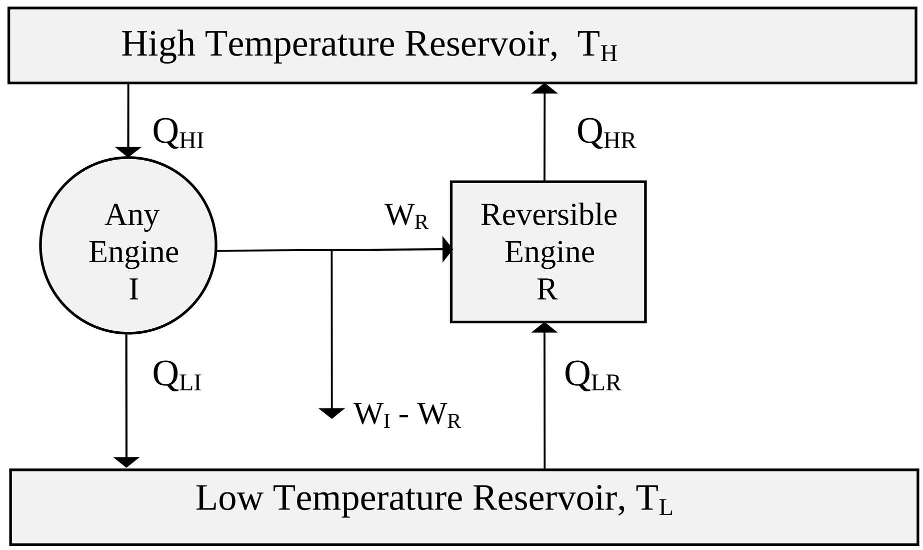
$$\eta_I = \frac{WI}{QH} > \eta_R = \frac{WR}{QH},$$

hence: $WI > WR$

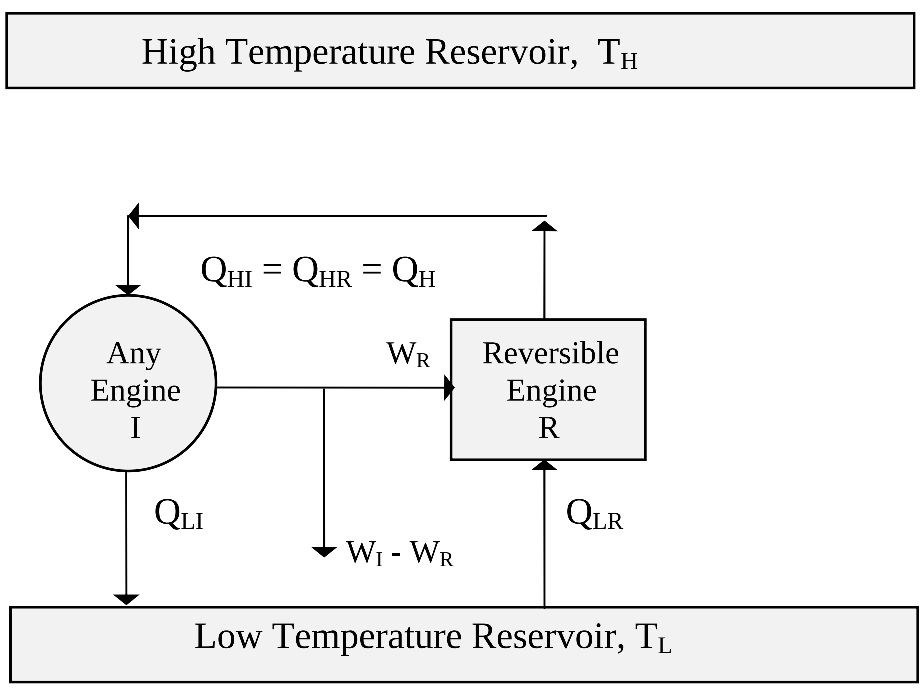
5) Reverse the reversible engine:



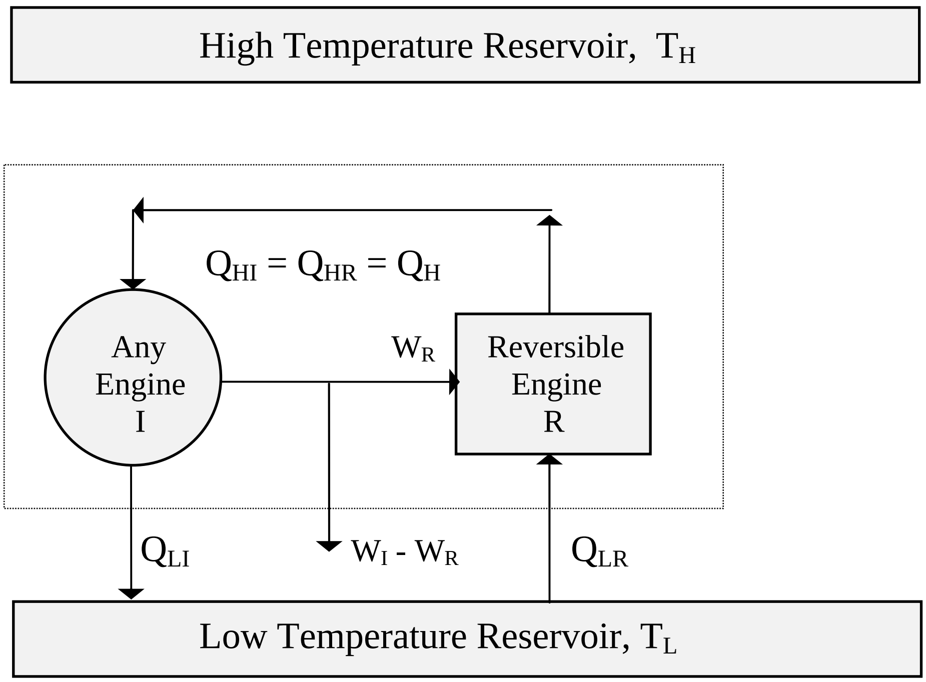
6) Since *WI* > *WR*, take part of *WI* and supply *WR*.



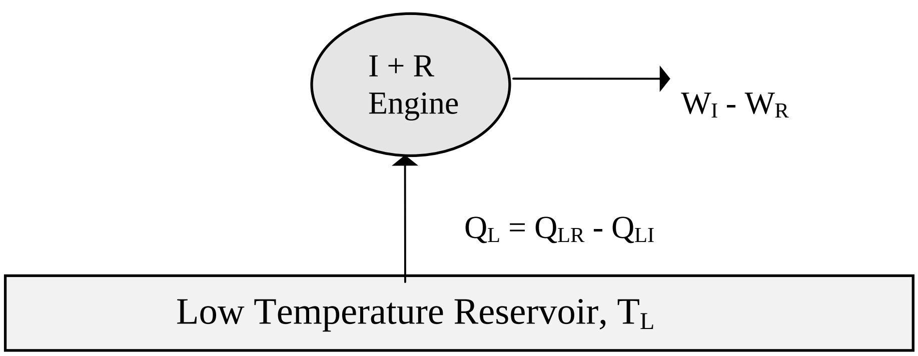
7) Use QHR to supply QHI, note that QHI = QHR = QH



8) Take the two engines as a single system.



9) Note that now we now have a single engine (system) which exchanges heat with a single reservoir T_L and produces net work $W_I - W_R$. This is a direct violation of the second law of thermodynamics.



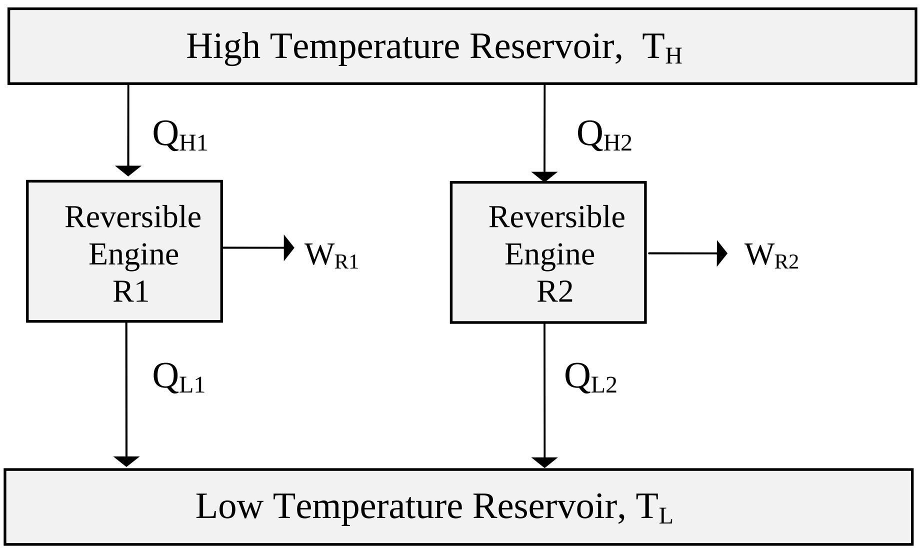
10) CONCLUSION: It is impossible to construct an engine that operates between two given reservoirs and is more efficient than a reversible engine operating between the same two reservoirs, i.e.

$$\eta_I \leq \eta_R$$

All reversible engines operating between the same temperature limits have the same efficiency.

Proof:

1) Take two reversible engines R1 and R2



2) Follow proof as above. Assume $\eta_{R1} > \eta_{R2}$

3) Reverse reversible engine R2 and let QH2 = QH1 = QH

4) This will lead to the conclusion that $\eta_{R1} \leq \eta_{R2}$

5) Next assume $\eta_{R2} > \eta_{R1}$

6) Reverse reversible engine R1 and let QH1 = QH2 = QH

7) This will lead to the conclusion that $\eta_{R2} \leq \eta_{R1}$

8) There is a contradiction unless $\eta_{R1} = \eta_{R2}$

NOTE: In the above no restrictions were placed upon the type of engine or system to be used or upon the details of the operation, hence the results are completely general.