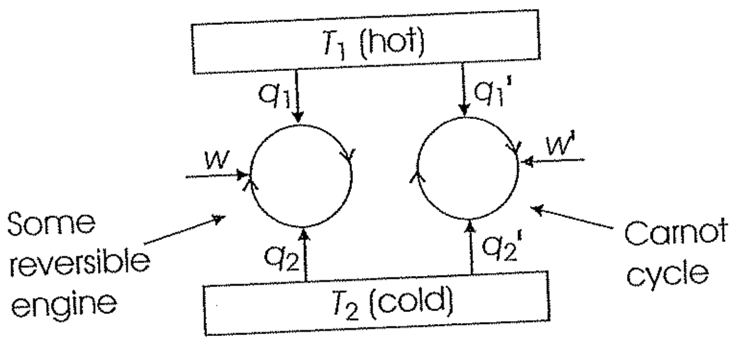
Entropy

- For a reversible ideal gas Carnot cycle:

Efficiency $$\varepsilon = \frac{-w}{q_{rev}} = 1 + \frac{q_2^{rev}}{q_1^{rev}} = 1 - \frac{T_2}{T_1}$$

$$\Rightarrow \frac{q_1}{T_1} + \frac{q_2}{T_2} = 0 \quad \Rightarrow \quad \oint \frac{đq_{rev}}{T} = 0$$

- The efficiency of any reversible engine has to be the same as the Carnot cycle:



Left $\quad \varepsilon = \frac{(-w)}{q_1}$

Right $\quad \varepsilon' = \frac{(-w')}{q_1'}$

<u>Assume</u> $\varepsilon' > \varepsilon$ (left engine less efficient than Carnot cycle)

Since the engine is reversible, we can run it backwards. Use the work ($-w'$) out of the Carnot engine as work input (w) to run the left engine backwards.

$\therefore$ Total work out = 0 $\quad (-w' = w > 0)$

But $\varepsilon' > \varepsilon \Rightarrow \frac{-w'}{q_1'} > \frac{-w}{q_1} \Rightarrow \frac{w}{q_1'} > \frac{-w}{q_1} = \frac{w}{-q_1} \Rightarrow q_1 < -q_1'$ since $q_1 < 0,\ q_1' > 0$

$$\Rightarrow \quad -(q_1' + q_1) > 0$$

This contradicts the 2nd law (Clausius). This says that we have a net flow of heat into the hot reservoir, but no work is being done!

$\therefore$ The efficiency of <u>any</u> reversible engine is $\varepsilon = 1 - \frac{T_2}{T_1}$

The Second Law

▲ First Law showed the equivalence of work and heat

$\Delta U = q + w$, $\oint dU = 0$ for cyclic process $\Rightarrow$ $q = -w$

Suggests engine can run in a cycle and convert heat into useful work.

▲ Second Law

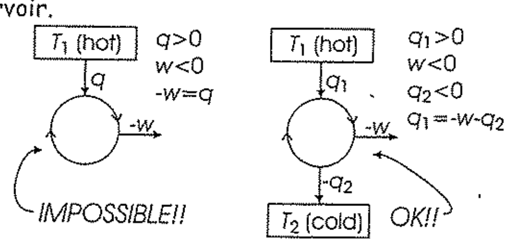
- Puts restrictions on useful conversion of q to w
- Follows from observation of a directionality to natural or spontaneous processes
- Provides a set of principles for
  - determining the direction of spontaneous change
  - determining equilibrium state of system

Heat reservoir Definition: A very large system of uniform T, which does not change regardless of the amount of heat added or withdrawn.

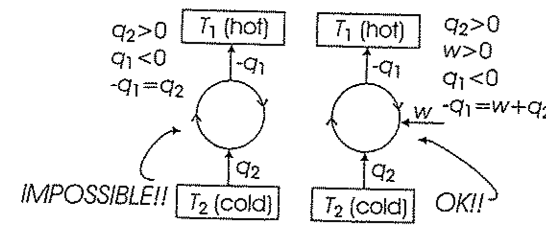
Also called heat bath. Real systems can come close to this idealization.

Different statements of the Second Law

Kelvin: It is impossible for any system to operate in a cycle that takes heat from a hot reservoir and converts it to work in the surroundings without at the same time transferring some heat to a colder reservoir.



Clausius: It is impossible for any system to operate in a cycle that takes heat from a cold reservoir and transfers it to a hot reservoir without at the same time converting some work into heat.



Alternative Clausius statement: All spontaneous processes are irreversible.

(e.g. heat flows from hot to cold spontaneously and irreversibly)

Mathematical statement: $\boxed{\oint \frac{đq_{rev}}{T} = 0 \quad and \quad \oint \frac{đq_{irrev}}{T} < 0}$

$\int \frac{đq_{rev}}{T}$ is a state function $= \int dS \quad \rightarrow \quad dS = \frac{đq_{rev}}{T}$

$S \equiv$ ENTROPY

$$\oint dS = 0 \quad \rightarrow \quad \Delta S = S_2 - S_1 = \int_1^2 \frac{đq_{rev}}{T} > \int_1^2 \frac{đq_{irrev}}{T}$$

for cycle $[1] \xrightarrow{irrev} [2] \xrightarrow{rev} [1]$

$$\int_1^2 \frac{q_{irrev}}{T} + \int_2^1 \frac{q_{rev}}{T} = \oint \frac{q_{irrev}}{T} < 0 \cdot$$

$$\int_1^2 \frac{q_{irrev}}{T} - \Delta S < 0 \Rightarrow \Delta S > \int_1^2 \frac{q_{irrev}}{T}$$