Classical Approach to 2nd Law for CM

- Start with observations about the ability to build devices (thermodynamic cycles)
- Clausius Statement of 2nd Law
  - concerns cycles that cause heat transfer from low temperature body to high temperature body (refrigerators and heat pumps)
- Kelvin-Planck Statement of 2nd Law
  - concerns cycles that use heat transfer to produce work/power (heat engines)
- Both observations can be shown to be "equivalent", violation of one equals violation of the other
- Can make other similar equivalent statements of 2nd Law

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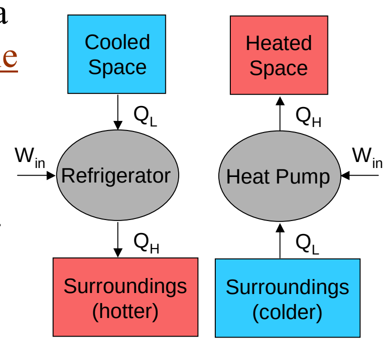
Clausius Statement of the 2nd Law

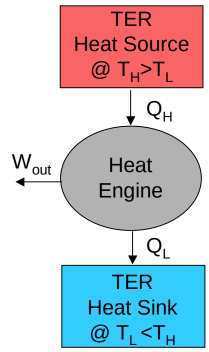
- It is impossible to construct a device that operates in a cycle and produces no effect on surroundings other than heat transfer from a lower temperature body to a higher temperature body (1850)
  - means refrigerators and heat pumps require work input (power)



Kelvin-Planck Statement of the 2nd Law

- It is impossible to construct a device that operates in a cycle and has no effect on surroundings other than producing a net work output and receiving (an equivalent amount of) heat transfer from a single Thermal Energy Reservoir (TER)
  - means heat engines must produce "waste" heat that must be transferred to surroundings

TER: fixed volume mass, only energy exchange as Q, and has uniform and (nearly) constant T



Carnot's Propositions

- How is temperature related to Second Law?
- Answer from examining reversible heat engines (classical example is Carnot cycle)
- Carnot's Propositions - corollaries of Clausius and Kelvin-Planck statements of 2nd Law
  1. It is impossible to construct a heat engine that operates between two TERs that has a higher thermal efficiency ($\eta_{th} \equiv W_{net,out}/Q_H$) than a reversible heat engine ($\eta_{th,irrev} < \eta_{th,rev}$)
  2. All reversible heat engines that operate between same two TERs have the same $\eta_{th,rev}$

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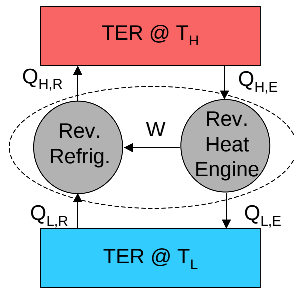
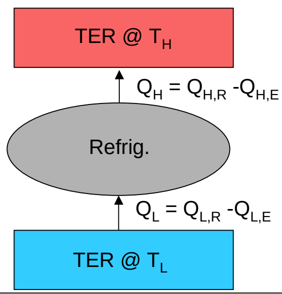
Proof of Carnot's Second Proposition

- Take two reversible devices, heat engine (E) that runs refrigerator (R) (refrig.=heat engine run backwards) using same TERs
- LET $\eta_{th,E} > \eta_{th,R}$ ($W/Q_{H,E} > W/Q_{H,R}$)





- $Q_{H,E} < Q_{H,R}$ (also $Q_{L,E} < Q_{L,R}$)
- But if call both devices one system, it looks like refrigerator with no work input - impossible

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Thermodynamic Temperature

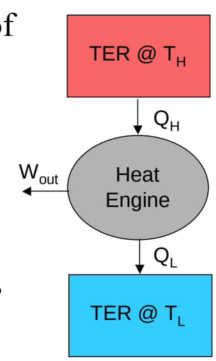
- Since $\eta_{th,rev}$ only depends on identity of TERs, only a function of absolute T

  $\eta_{th,rev} = \eta(T_H,T_L)$
- Rewrite efficiency, use 1st Law

  $$\eta_{th} = W_{net,out}/Q_H = (Q_H - Q_L)/Q_H$$

  $$\eta_{th} = 1 - Q_L/Q_H$$
- Apply this to many reversible engines, implies $[Q_L/Q_H]_{rev} = f(T_L)/f(T_H)$
  - chose def'n. of thermodynamic T

    $[Q_L/Q_H]_{rev} = T_L/T_H$,
  - use in η, $\boxed{\eta_{th,rev} = 1 - T_L/T_H}$ **Carnot Efficiency** - true for totally rev. heat engines



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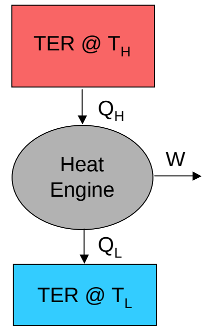
Clausius Inequality, Entropy, and 2nd Law



- Consider any reversible heat engine

$$\oint \frac{\delta Q}{T}\bigg|_{rev} = \oint_{\substack{\text{heat}\\\text{addition}}} \frac{\delta Q}{T} + \oint_{\substack{\text{heat}\\\text{rejection}}} \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

- Since cyclic integral of $\delta Q/T$ is zero must be a thermodynamic property, **entropy**

$$dS = \frac{\delta Q}{T}\bigg|_{rev}$$

- From Carnot's 1st Proposition, can show

$$\oint \frac{\delta Q}{T}\bigg|_{irrev} < 0, \text{ or in general } \boxed{\oint \frac{\delta Q}{T} \le 0}$$ **Clausius Inequality**

$$\boxed{dS \ge \frac{\delta Q}{T}}$$ **2nd Law for Control Mass**