

ABE 201

Biological Thermodynamics 1

Module 11

Introduction to Entropy

Outline

- Introduction to the 2nd Law of Thermodynamics
- Introduction of entropy as a concept.
- Heat engines and cycles
- Maximum thermal efficiency and entropy

2nd Law of Thermodynamics

- A process must satisfy 1st law to occur, but a process obeying 1st law DOES NOT mean it will actually occur.

Example 1



Heat is transferred between the cup and the cold ambient

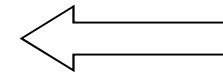


$$T_{\text{amb}} < T_{\text{coffee}}$$

Satisfies the First and the Second law of Thermodynamics



Heat



Satisfies the First Law, but it cannot take energy of the **Cold Ambient** and add back to heat the coffee

$$\Delta U + \Delta E_k + \Delta E_p = Q - W$$

First Law Satisfied in **both** cases as long as energy balances
(direction not important)

2nd Law of Thermodynamics

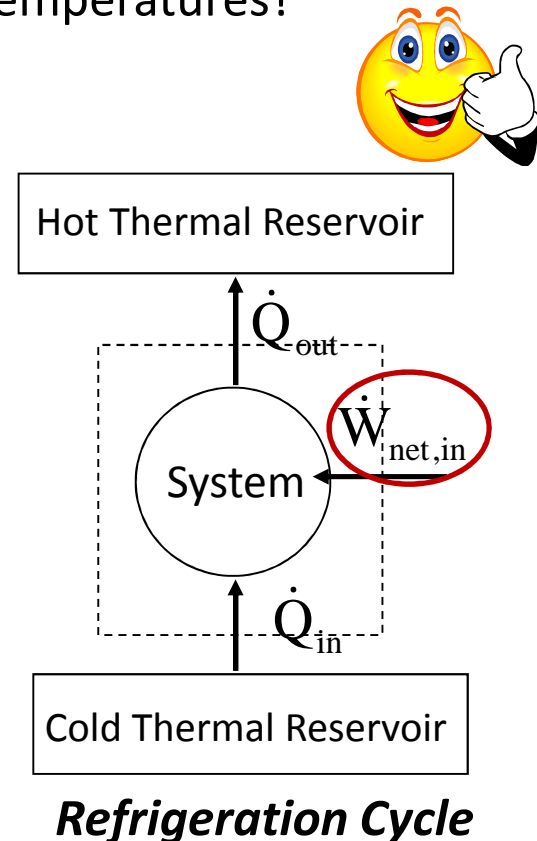
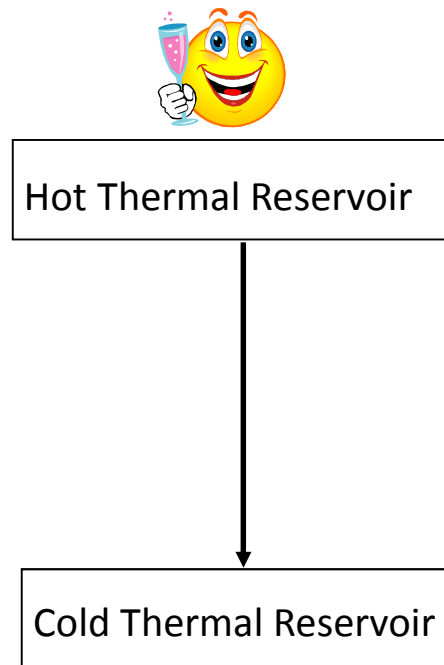
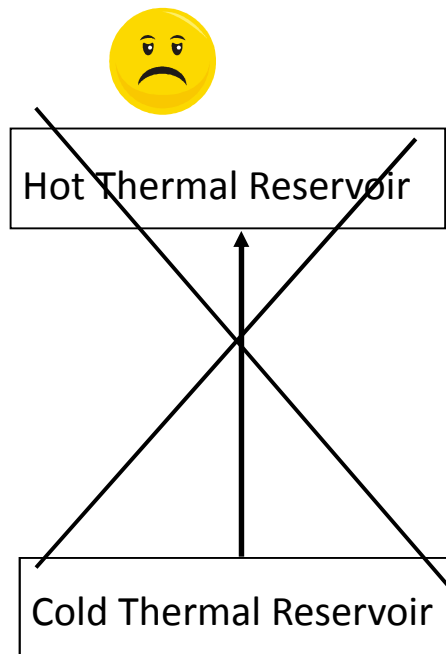
- Identify the direction of a process
- Determines the theoretical limits for the performance of commonly used engineering systems (heat engines, refrigerators)
- Asserts energy has quality not only quantity

Clausius Statement

→ concerns cycles that cause heat transfer from low temperature body to high temperature body (refrigerators and heat pumps)

→ *No process is possible whose sole result is the transfer of heat from a colder to a hotter body.*

Could we transfer heat from low to high temperatures?



Developing the Concept of Entropy

- Need a state variable that describes a property of a substance that is independent of prior history of the substance
 - State variables: T , P , spec. V , U , H
- This state variable should be independent of other state variables, but relatable to other state variables
- This state variable must be useful for determining directionality of spontaneous thermodynamic processes

Entropy, S

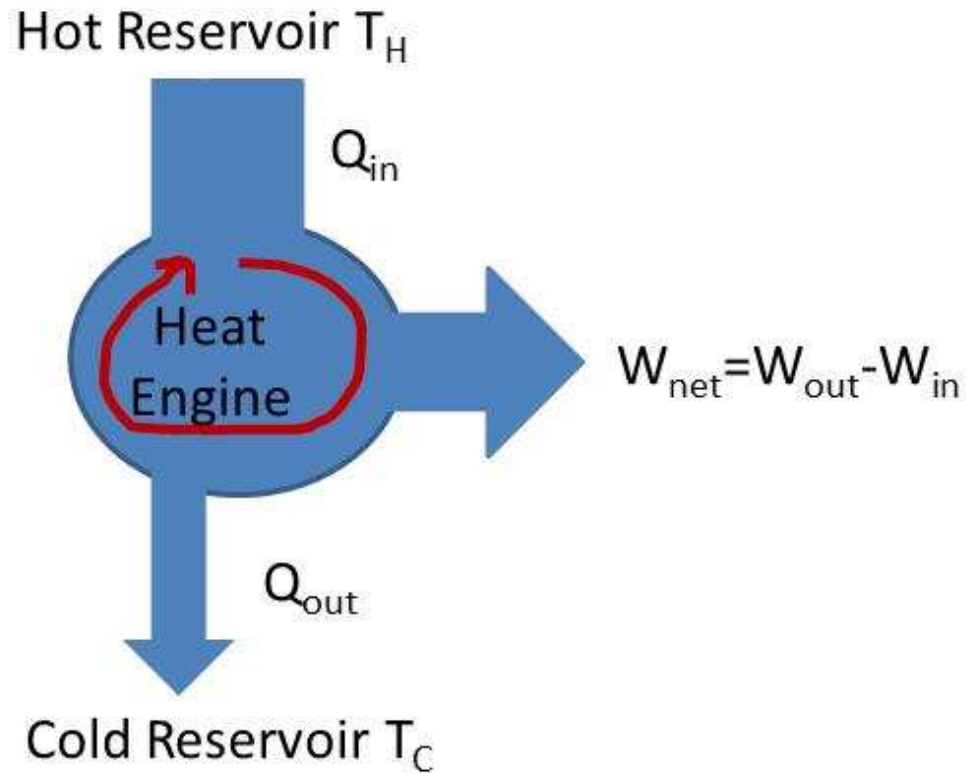
- *Entropy* (S) is a term coined by Rudolph Clausius in the 19th century.
- Originated from the heat engine concept.
- defined as the ratio of heat delivered and the temperature at which it is delivered.

- $S = \frac{Q}{T}$ Entropy has units of energy per temperature = J/K

$$dS = \frac{\partial Q}{T}$$

The unit of the Clausius was proposed, but didn't catch on: 1 Cl = 4.184 J/K

Heat Engine



Think the heat engine as a “black box” containing a working fluid which accepts heat from a high temperature source, turns some into work, and rejects the remainder to a low temperature sink, operating on a cycle.

Thermal Energy Reservoir

A (hypothetical) body with a large thermal energy capacity that can absorb or supply finite amounts of heat without undergoing a change in temperature.

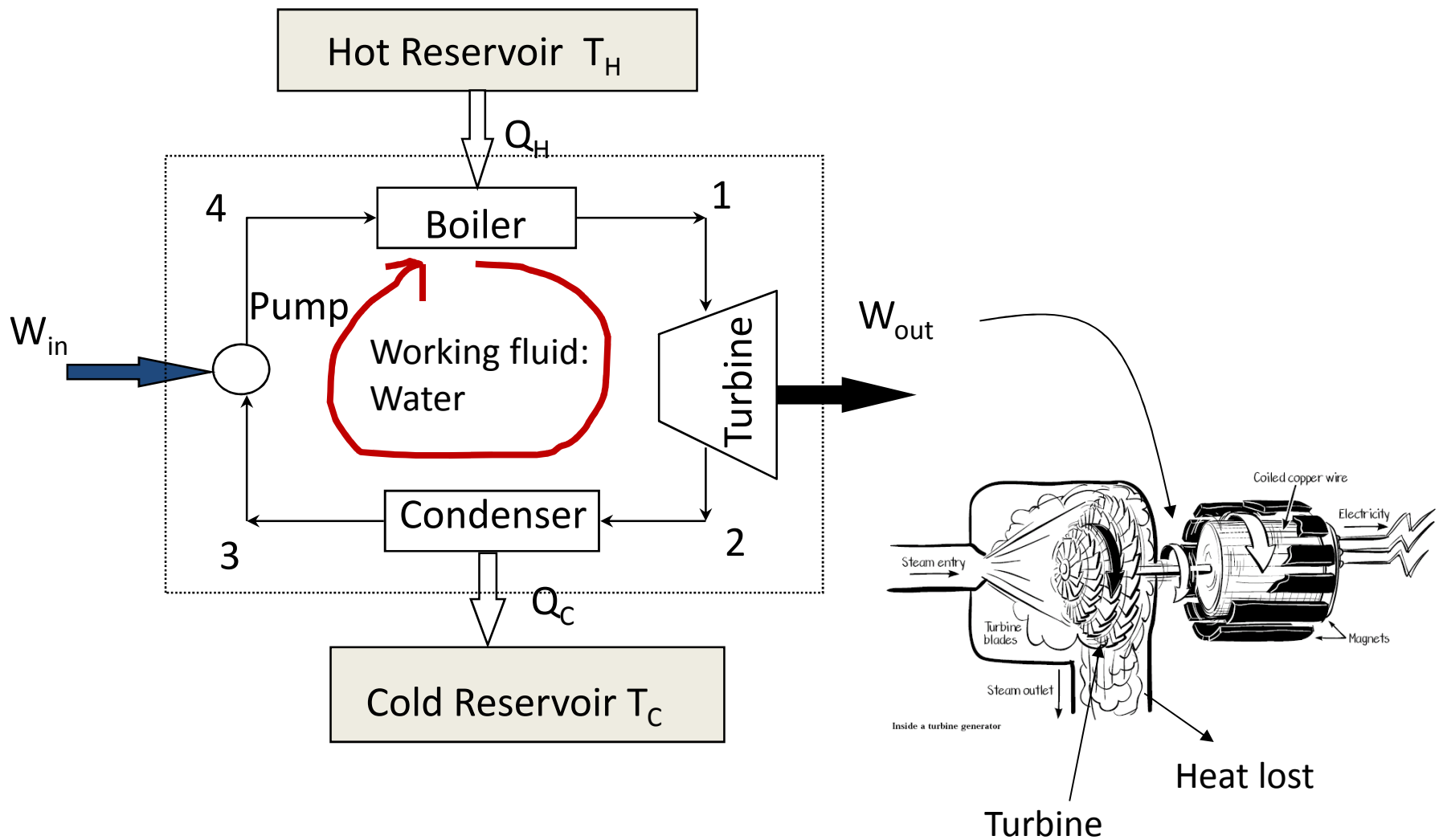
Hot reservoir (heat source): A reservoir that supplies heat energy.
Sun, a furnace, a person in a small room

Cold reservoir (heat sink): A reservoir that absorbs heat energy.
Atmosphere, river, lake, ocean, the room surrounding a refrigerator

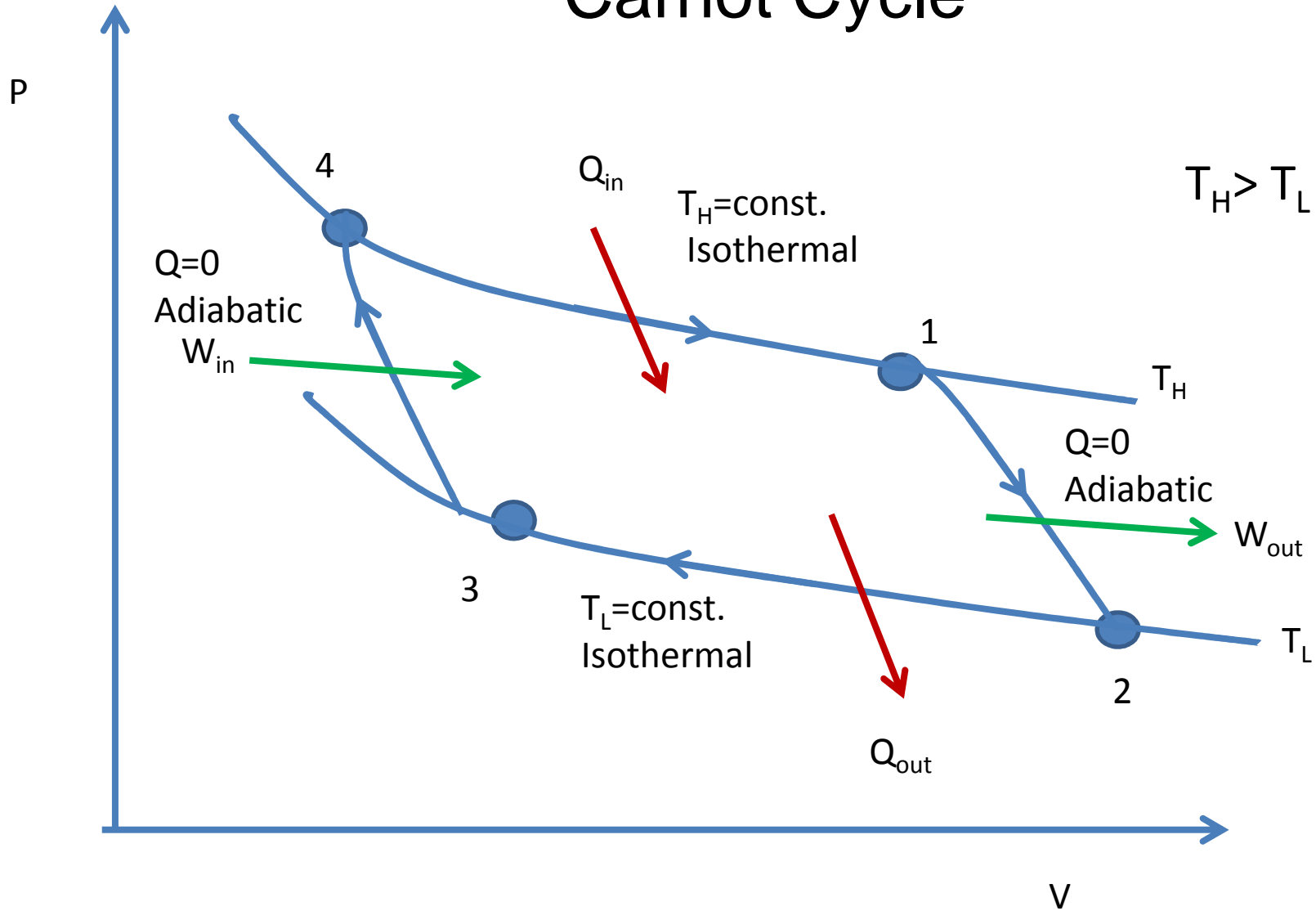
Steam Power Plant-Heat Engine

Thermodynamic Cycles

POWER CYCLE



Carnot Cycle



Steam Power Plant-Heat Engine

The water substance that flows through the four components proceeds through a thermodynamics cycle because the water continually retraces the same change in state, i.e. it comes to the original initial state once a cycle is completed.

1. Mass balance : No mass in, No mass out
2. 1st law energy balance:
the 1st law energy balance of water in this cycle,

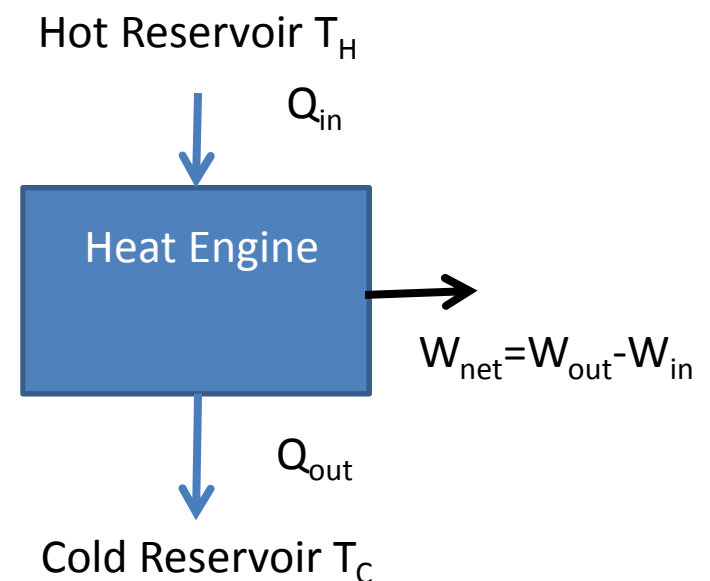
$$\Delta U + \Delta E_k + \Delta E_p = (Q_{in} - Q_{out}) - (W_{out} - W_{in})$$

$$\Delta U, \Delta E_k, \Delta E_p = 0, \quad 0 = (Q_{in} - Q_{out}) - (W_{out} - W_{in})$$

$$(Q_{in} - Q_{out}) = (W_{out} - W_{in})$$

However, the 1st law of thermodynamics does not tell us the how much heat is converted to work, how much heat is thrown away, direction of energy flow, what is the efficiency of the engine.

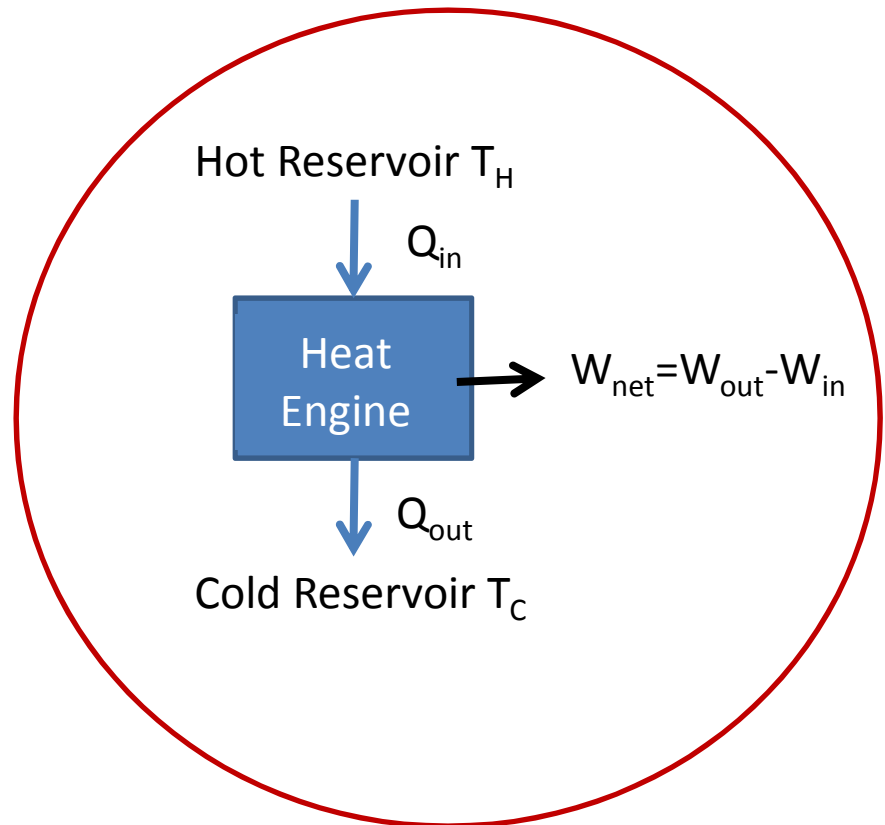
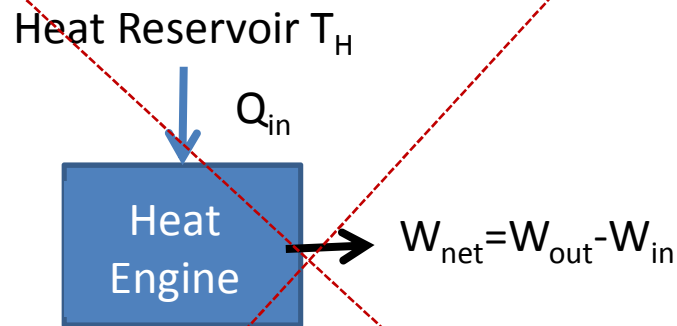
→ 2nd law of thermodynamics is introduced!



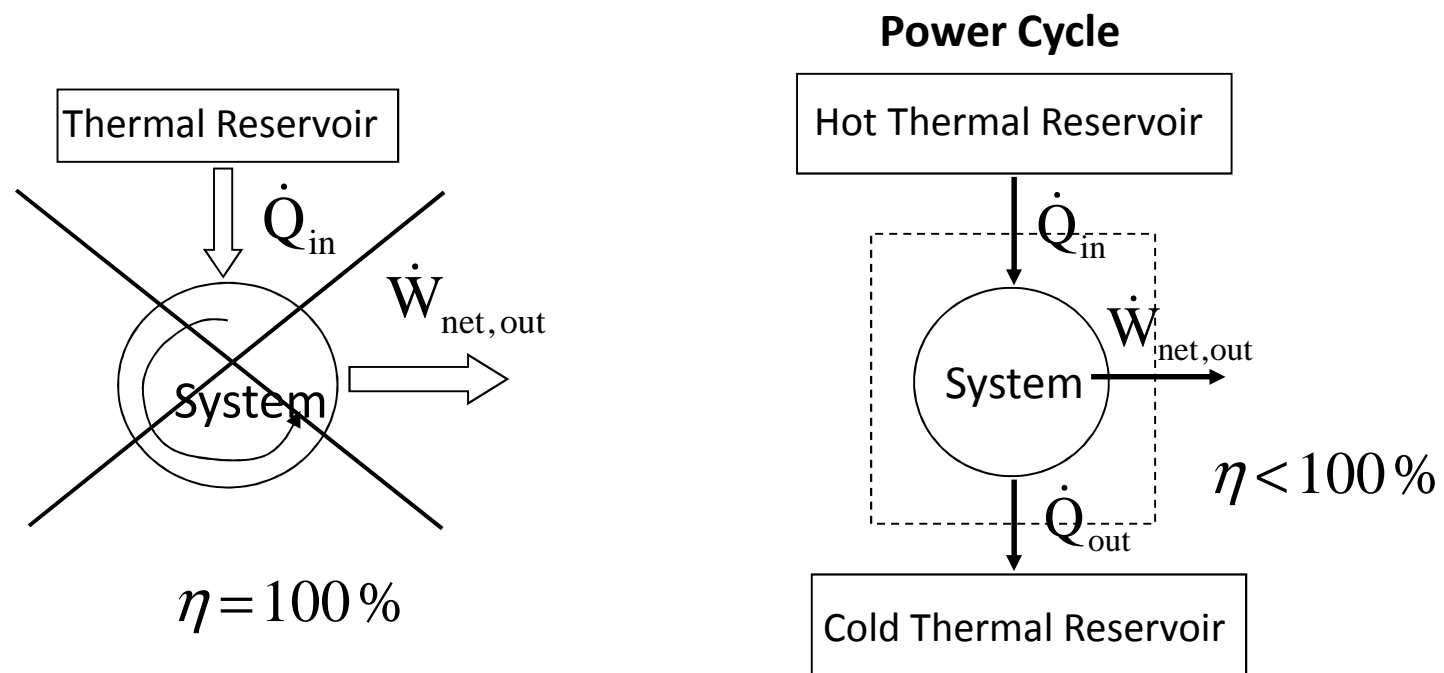
Kelvin Planck Statement

→ concerns cycles that use heat transfer to produce work/power (heat engines)

→ No process on a cyclic operation is possible to convert all heat to work



Reversible and Irreversible Processes



- The Kelvin-Planck statement requires that the thermal efficiency of **all heat engines must be less than 100%** but the limiting maximum value has to be set.
- An ideal heat engine (power cycle or refrigeration cycle) sets the theoretical maximum thermal efficiency.
- Idealized process= Reversible Process
- The introduction of **the concept of reversibility and irreversibility** must be introduced.

Thermal Efficiency of Heat Engine

$$\text{Performance} = \text{Efficiency} = \frac{\text{Desired Output}}{\text{Required Input}}$$

$$\eta = \frac{W_{net,out}}{Q_{in}} = \frac{\dot{W}_{net,out}}{\dot{Q}_{in}}$$

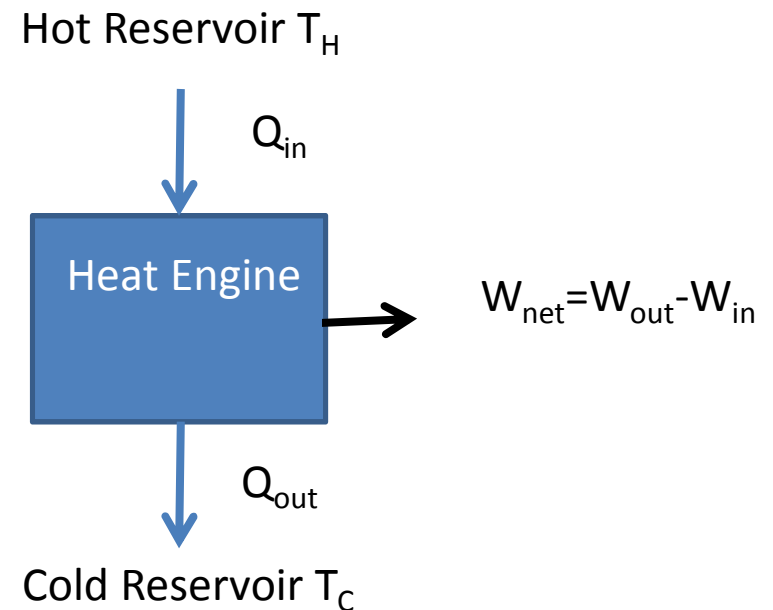
By 1st Law of Thermodynamics

$$\Delta U = Q - W$$

$$\Delta U = 0$$

$$W_{out} - W_{in} = Q_{in} - Q_{out}$$

$$\eta_{Th} = \frac{W_{out} - W_{in}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} < 1$$



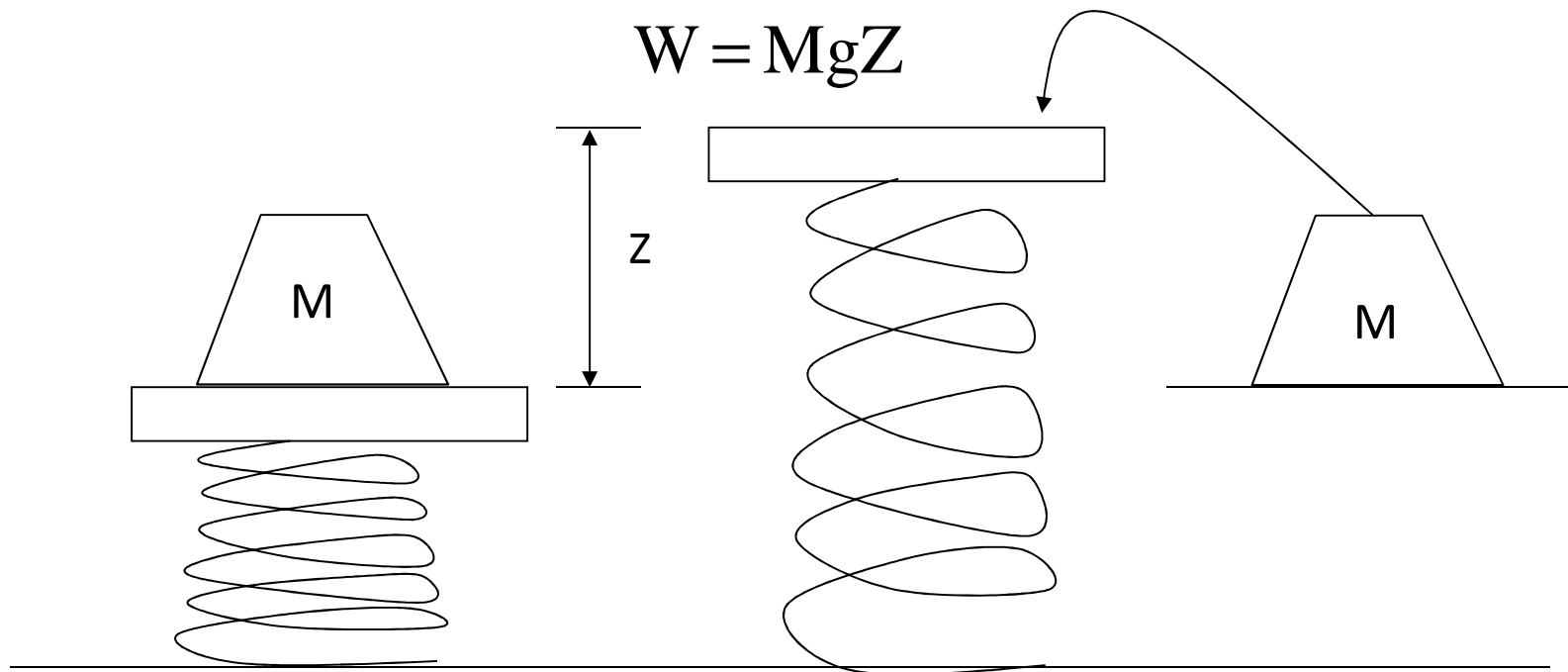
Reversible vs. Irreversible

- Reversible process: a process that can be reversed to its original state without leaving any trace on the system and surroundings. Does not occur in nature. Idealization of an actual process. Changes are infinitesimally small in a reversible process.
- Irreversible process cannot be undone by exactly reversing the change to the system.
- **All Spontaneous processes are irreversible.**
- **All Real processes are irreversible.**
- Reversible process is easy to analyze, **serves as an ideal process to which an actual process can be compared, and gives a theoretical limits for an actual process.**

REVERSIBLE AND IRREVERSIBLE PROCESSES

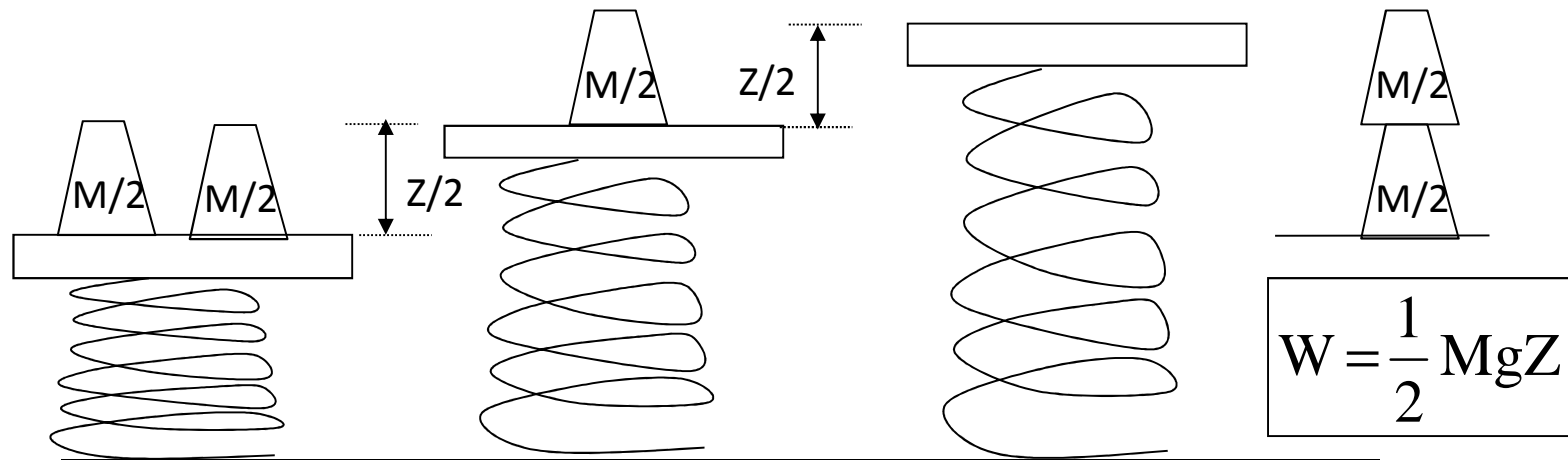
A process commencing from an initial equilibrium state is called totally reversible if at any time during the process both the system and the environment with which it interacts can be returned to their initial states

Experiment 1

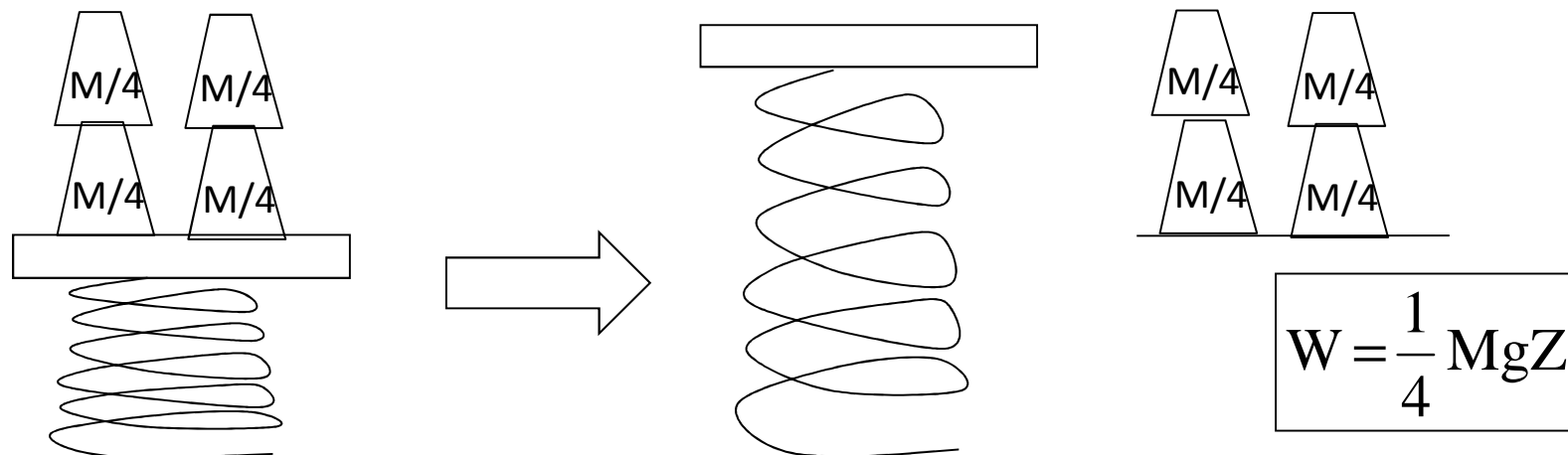


REVERSIBLE AND IRREVERSIBLE PROCESSES

Experiment 2

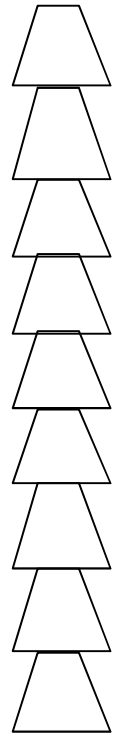
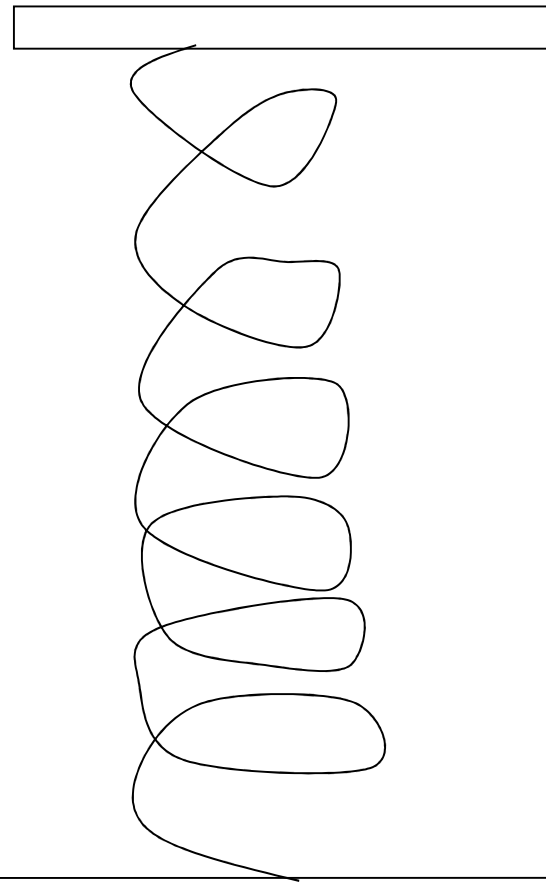
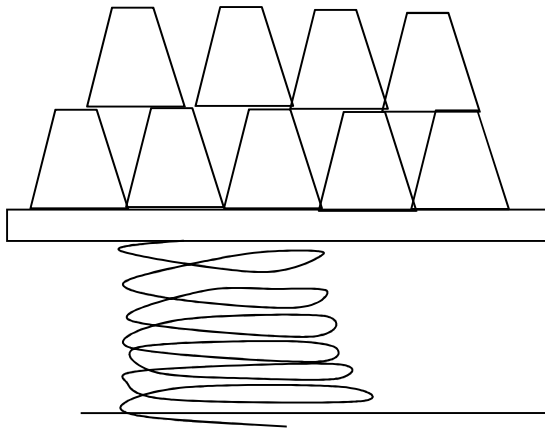


Experiment 3



REVERSIBLE AND IRREVERSIBLE PROCESSES

$$W = \frac{1}{n} MgZ$$

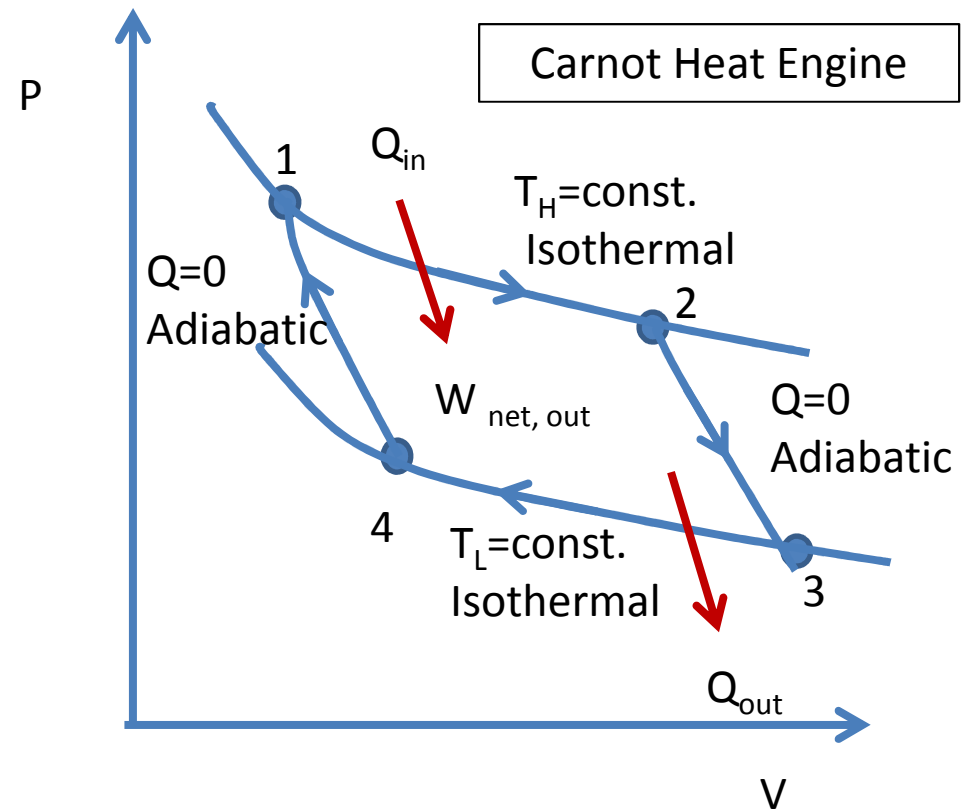
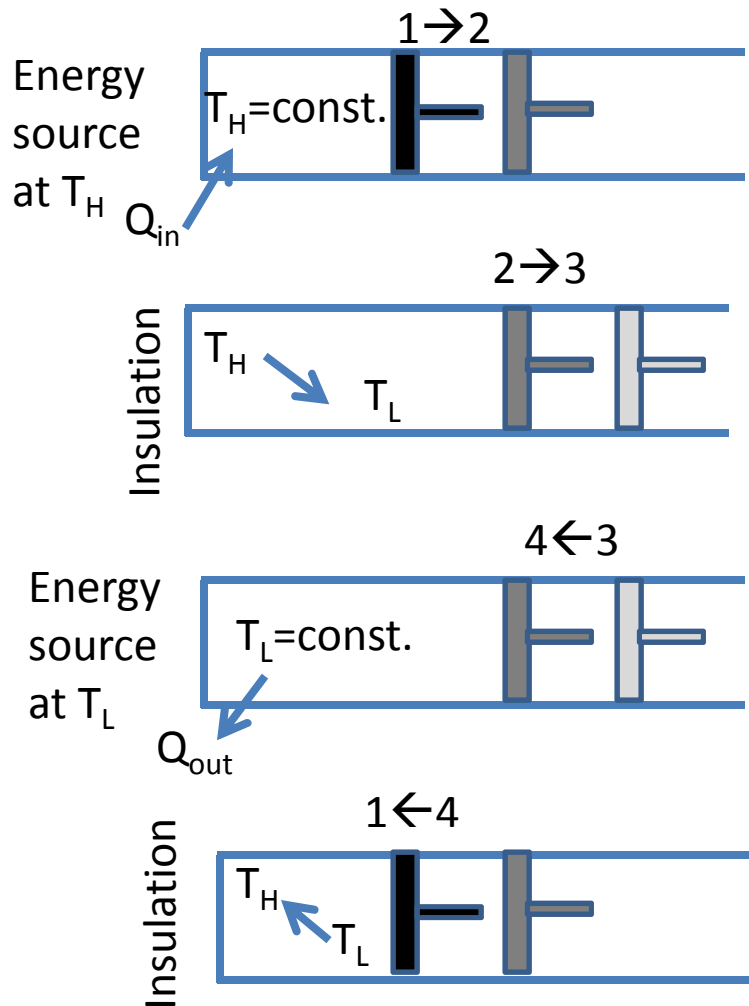


$$\lim_{n \rightarrow \infty} W = 0$$

← REVERSIBLE PROCESS

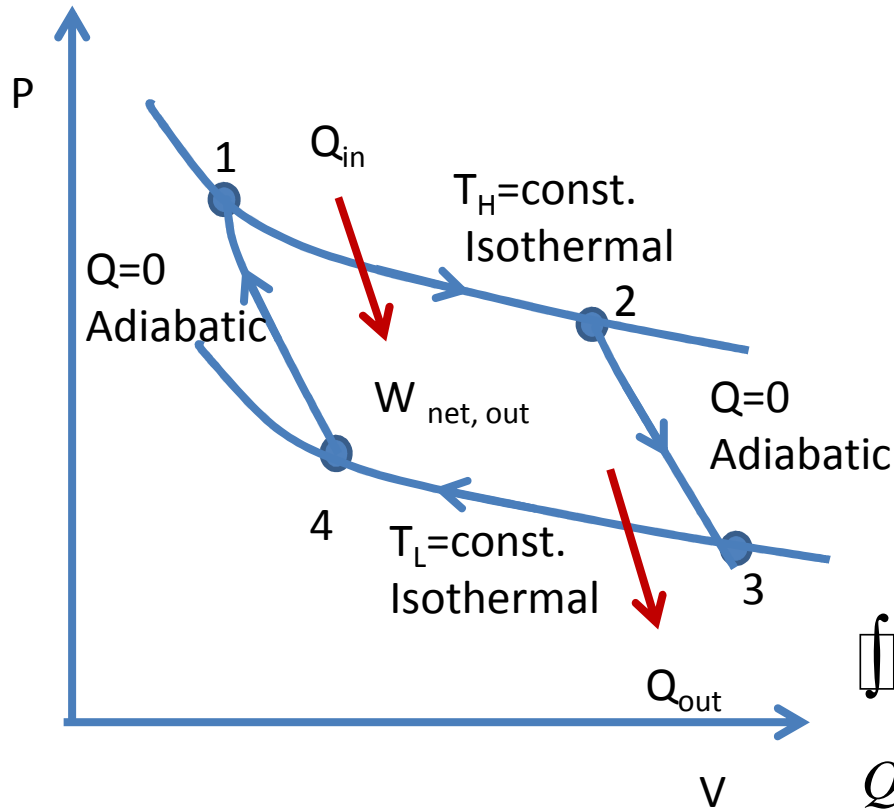
Carnot Cycle

- Most efficient cycles are reversible cycles
- Provides upper limits on the performance of real cycles
- Carnot cycle is the best known reversible cycle (theoretical, idealized process)



Reversed Carnot Cycle = Carnot Refrigeration

Reversible Heat Engine Cycles determine the Maximum Efficiency



Thermal efficiency of a reversible heat engine cycle (Carnot cycle)

=Maximum efficiency of a real cycle operating between the two thermal reservoirs at T_H and T_L

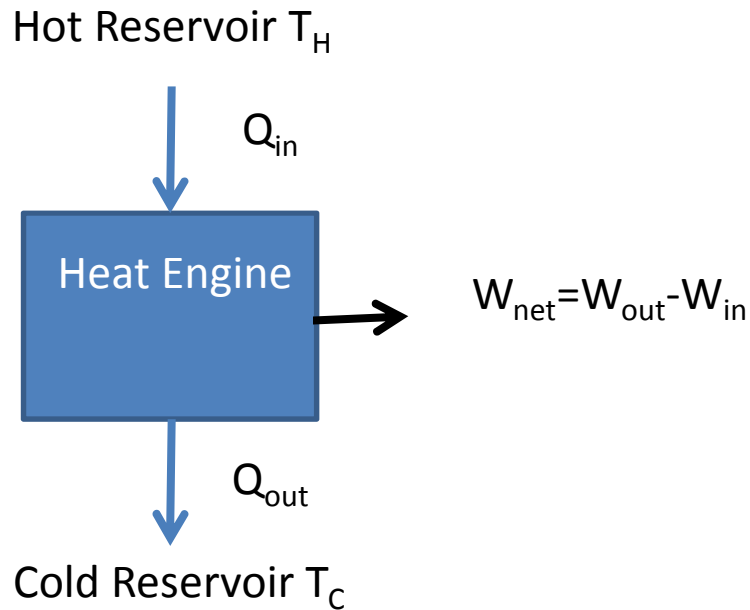
$$\oint \frac{\delta Q}{T} = \frac{Q_{in}}{T_H} + 0 - \frac{Q_{out}}{T_L} - 0 = 0$$

$$\frac{Q_{in}}{T_H} - \frac{Q_{out}}{T_L} = 0,$$

$$\frac{Q_{in}}{T_H} = \frac{Q_{out}}{T_L}, \quad \frac{Q_{out}}{Q_{in}} = \frac{T_L}{T_H}$$

$$\eta_{Th} = \frac{W_{out} - W_{in}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{T_L}{T_H} < 1$$

Reversible Heat Engine Cycles determine the Maximum Efficiency



$\eta < \eta_{reversible} : irreversible$

$\eta = \eta_{reversible} : reversible$

$\eta > \eta_{reversible} : impossible$

Irreversible Cycle

$$\eta_{irreversible} = \frac{W_{net,out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

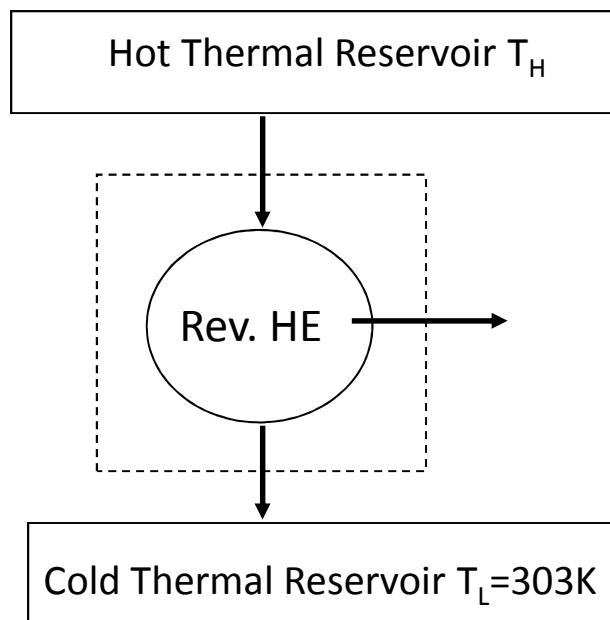
Reversible Cycle

$$\eta_{reversible} = 1 - \frac{Q_{in}}{Q_{out}} = 1 - \frac{T_L}{T_H}$$

Kelvin Temperature Scale

How do we increase η ?

$$\eta_{reversible} = 1 - \frac{T_L}{T_H}$$



T_H	$\eta_{reversible}$
925K	67.2%
700K	56.7%
350K	13.4%

↑
Quality of
energy

Summary

- 1st Law of Thermodynamics = conservation of energy
- 2nd Law of Thermodynamics = direction of processes (arrow of time)
- Entropy is a state property that is useful for applying the 2nd Law
- Efficiency of thermal processes is linked to the concept of entropy