ABE 201
Biological Thermodynamics 1

Module 11

Introduction to Entropy

Summary

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

1st Law of Thermodynamics

- Conservation of energy (all types)

- Balances conversion of energy and transfer of energy

- Accounting of the <u>quantity</u> of energy

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

$$\Delta \dot{H} + \Delta \dot{E}_k + \Delta \dot{E}_p = \dot{Q} - \dot{W}_s$$

2nd Law of Thermodynamics

- Identify the <u>direction</u> of a process

- Determines the theoretical limits for <u>efficiency</u> of energy transformations

- Assigns <u>quality</u> to energy

- Energy has both quality (entropy) and quantity (enthalpy)

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

Entropy has units of energy per temperature

$$\frac{J}{K}, \frac{kJ}{K}, \frac{BTU}{{}^0R}, \frac{Cal}{K}, \frac{erg}{K}, \frac{hp \cdot day}{{}^0R}, \frac{kW \cdot h}{K}, Cl$$

While Clausius (Cl) isn't a common unit, it's <u>mentally</u> useful for thinking about entropy as a <u>new</u> category of unit.

Energy = $\frac{kg \cdot m^2}{s^2}$ = ??? $= J$

Entropy = $\frac{J}{K} = \frac{kg \cdot m^2}{s^2 \cdot K}$ = ??? $= Cl$

Entropy

Entropy is **<u>not</u>** a measure of the <u>disorder</u> or <u>chaos</u> in a system (except in a very limited definition of disorder/order)

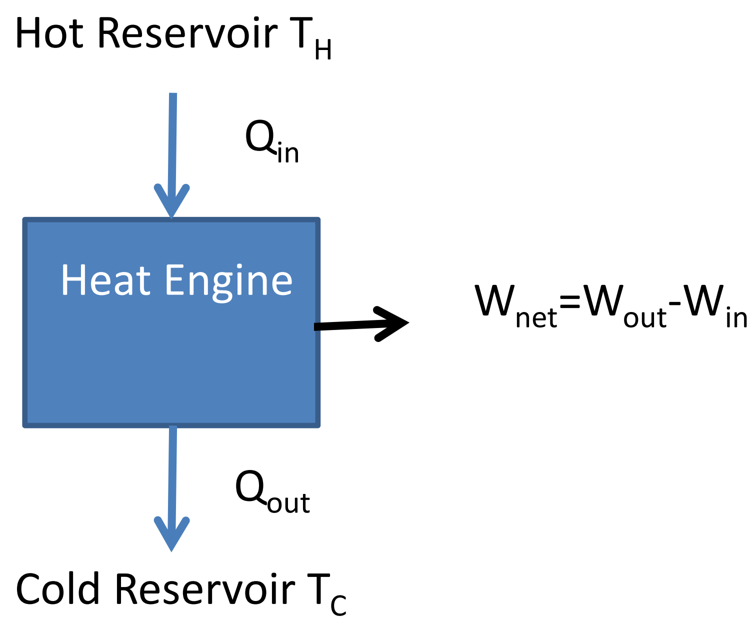
$\frac{kg}{m^3}$ = concentration is the how **<u>compact</u>** the <u>mass</u> is in a system

$\frac{J}{K}$ = entropy is a measure of the **<u>dispersion</u>** of <u>energy</u> in a system (opposite of compact)

Spontaneous changes are always accompanied by a dispersal of energy (increase in entropy)

Thermal Efficiency of Heat Engine

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



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

By 1st Law of Thermodynamics

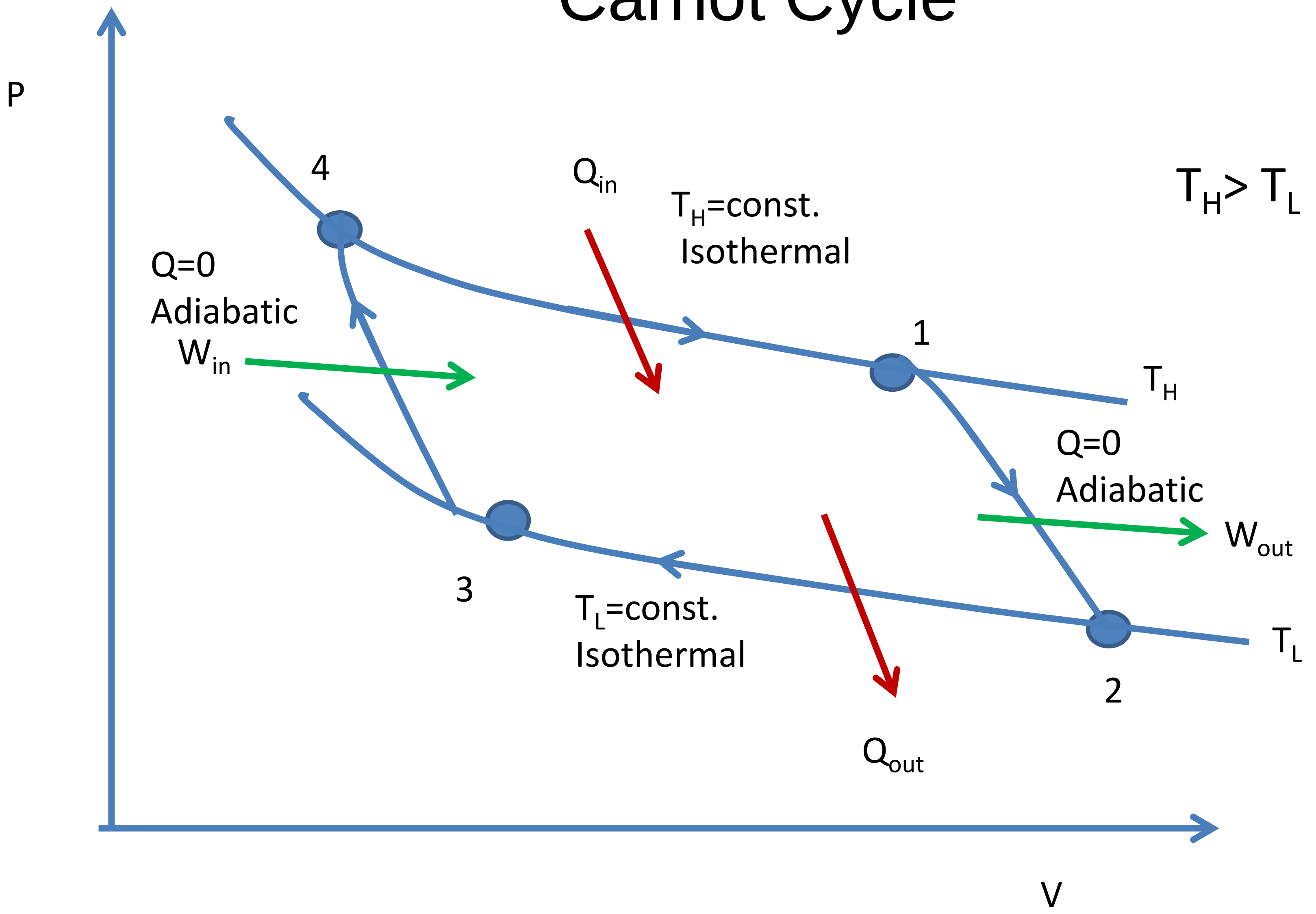
$$\Delta U = Q - W$$

$$\Delta U = 0$$

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

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

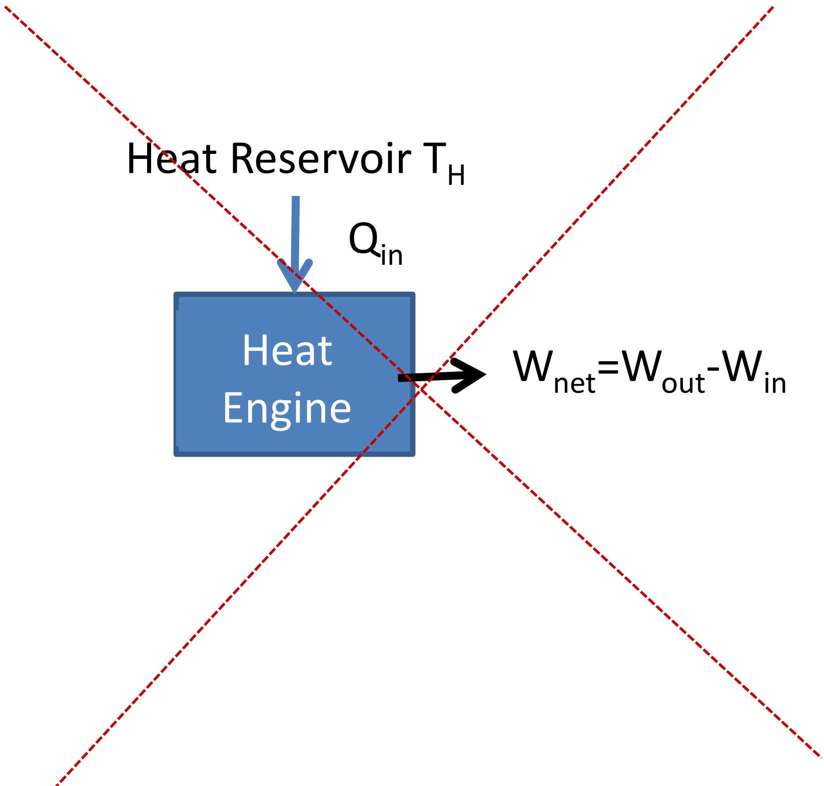
Carnot Cycle

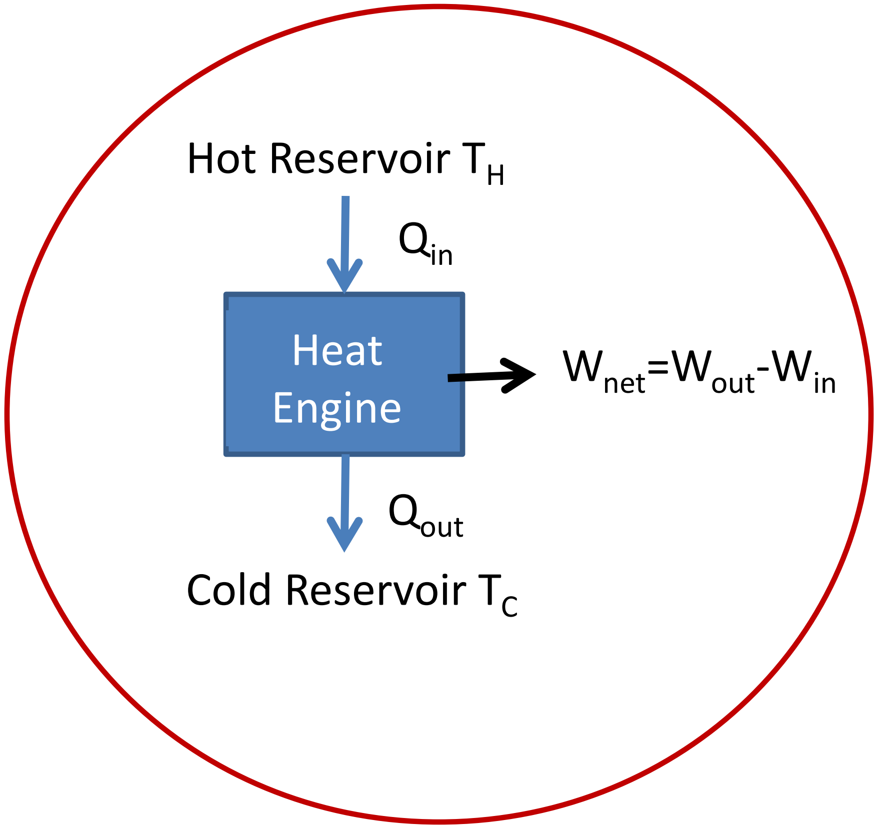


Kelvin Planck Statement

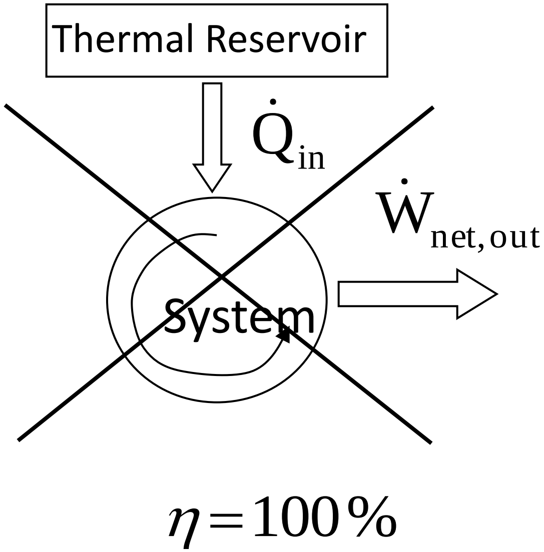
→concerns cycles that use heat transfer to produce work/power (heat engines)

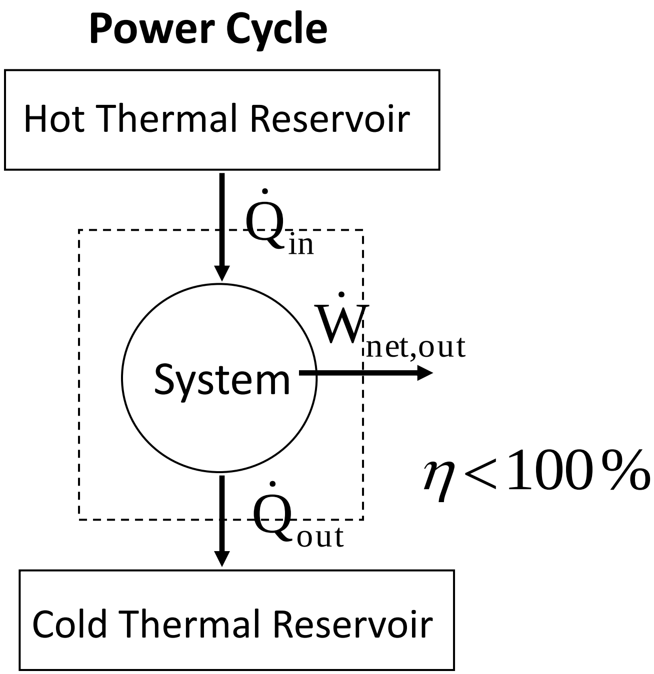
→No process on a cyclic operation is possible to convert all heat to work





Reversible and Irreversible Processes





- The Kelvin-Planck statement requires that the thermal efficiency of **all heat engines must be less than 100%** but the <u>limiting maximum value has to be set</u>.
- 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.

Reversible vs. Irreversible

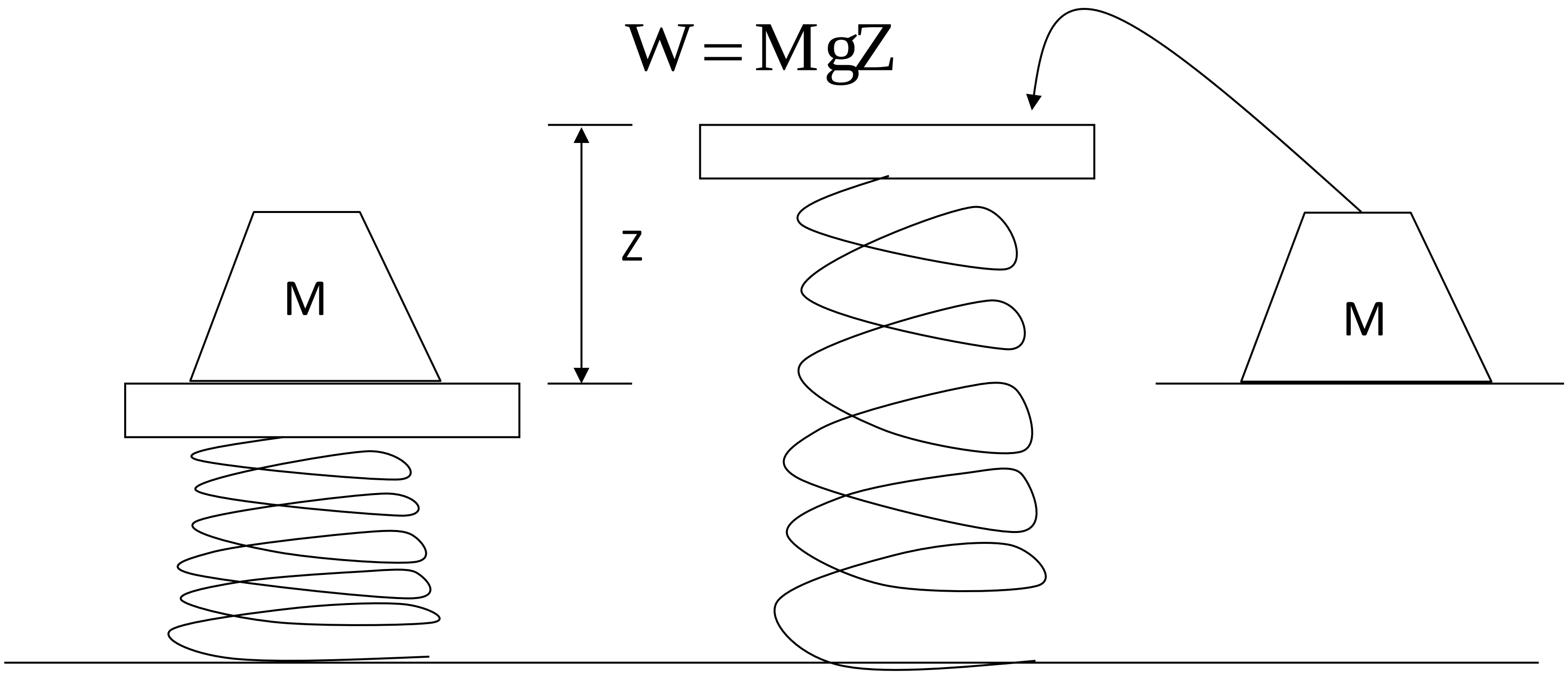
- Reversible process: a process that can be reversed to its original state without leaving any trace on the system and surroundings. Does not occur in nature. Idealization of an actual process. Changes are infinitesimally small in a reversible process.
- Irreversible process cannot be undone by exactly 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

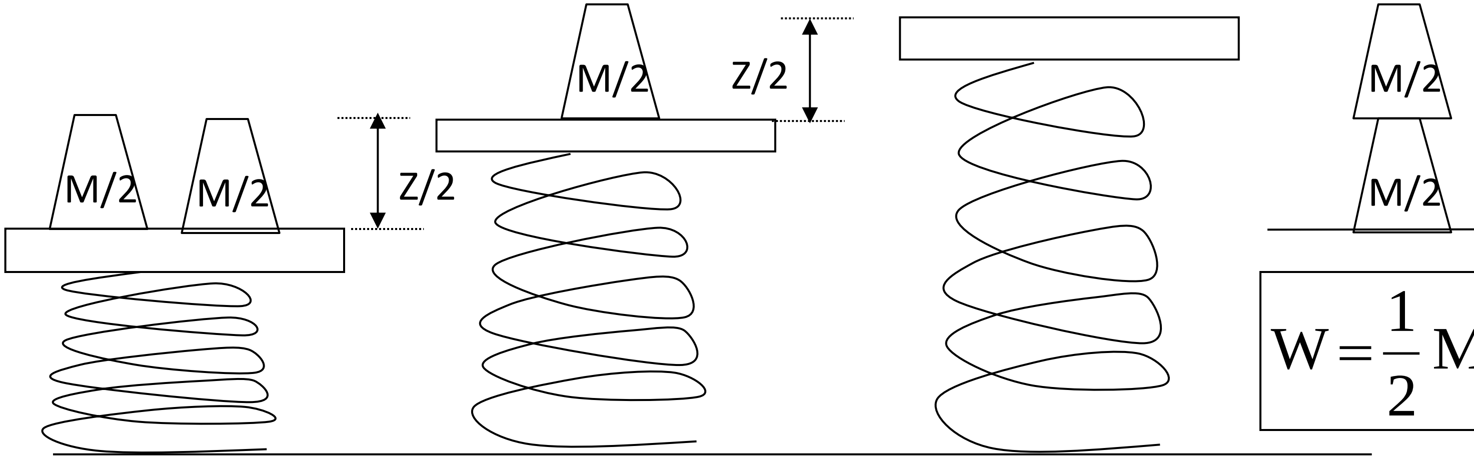
<u>Experiment 1</u>

$$W = MgZ$$



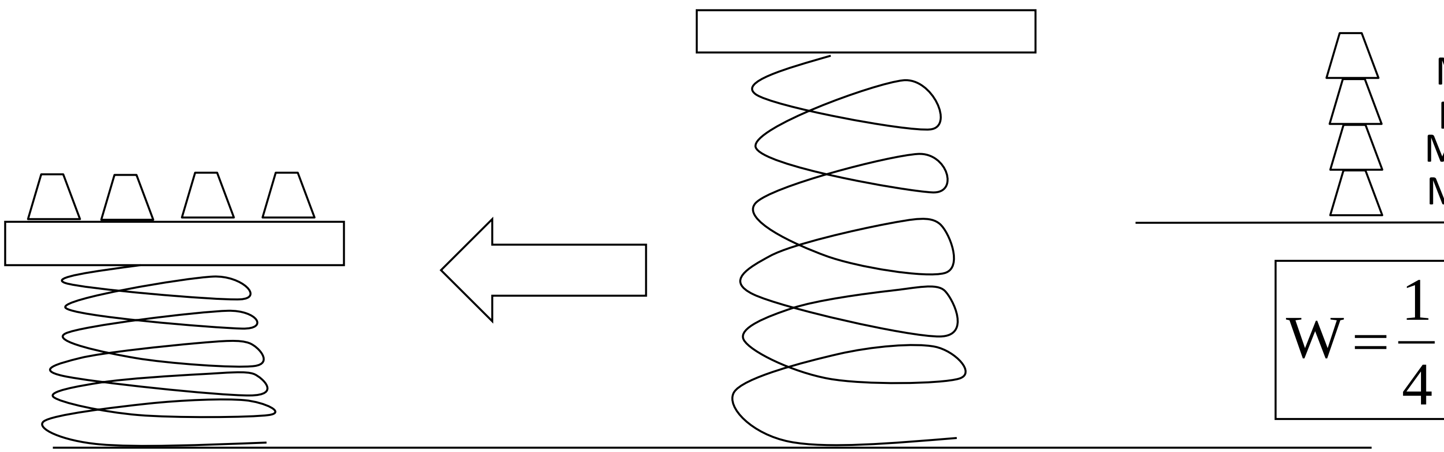
REVERSIBLE AND IRREVERSIBLE PROCESSES

Experiment 2



$$W = \frac{1}{2} MgZ$$

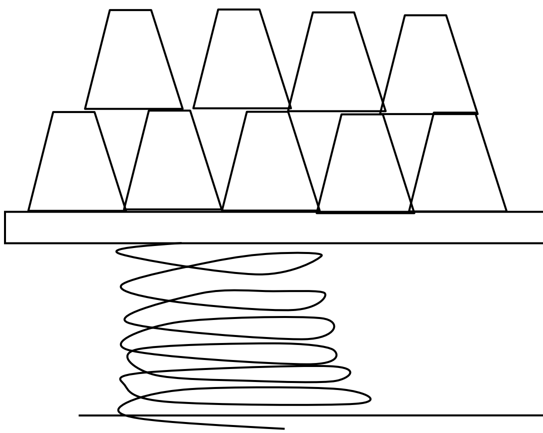
Experiment 3

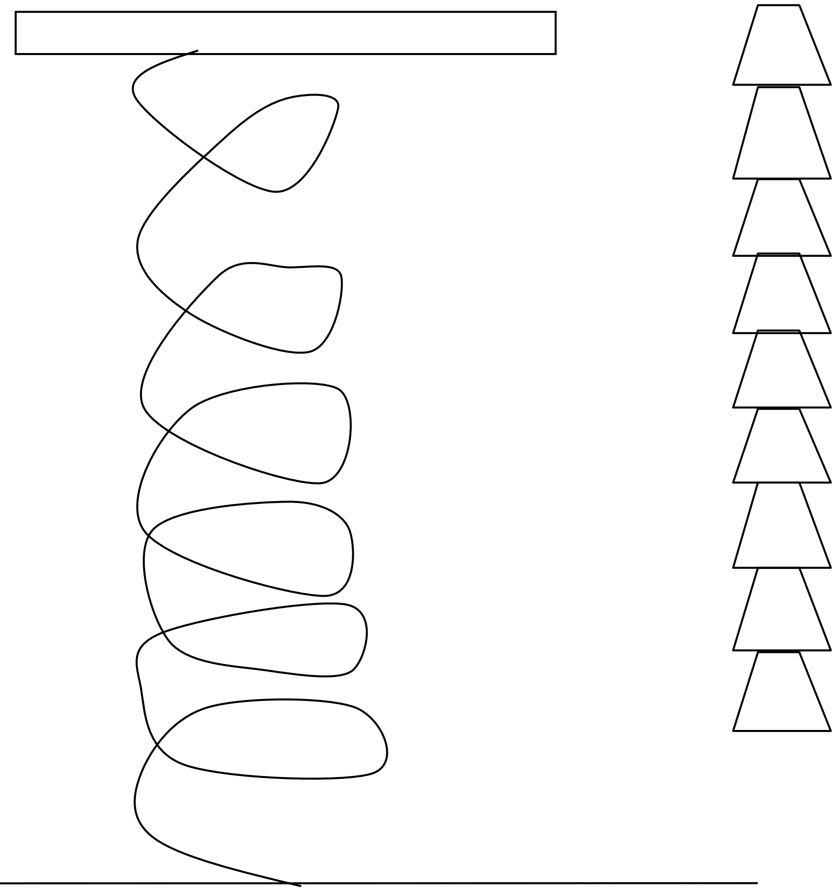


$$W = \frac{1}{4} MgZ$$

REVERSIBLE AND IRREVERSIBLE PROCESSES

$$\boxed{W = \frac{1}{n} M g Z}$$

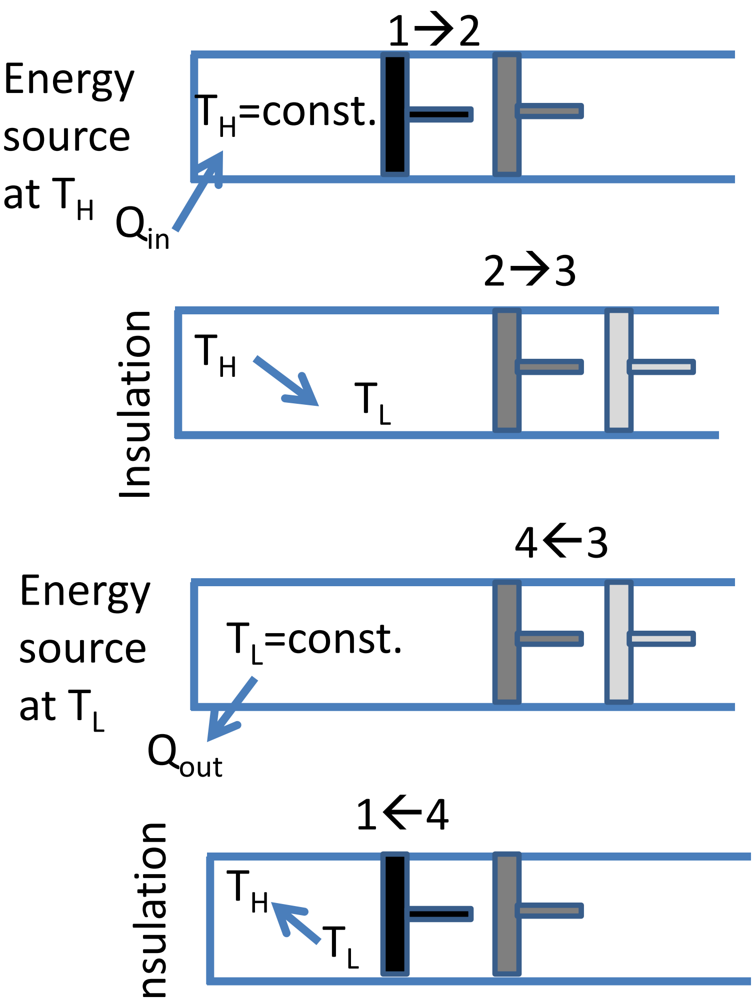


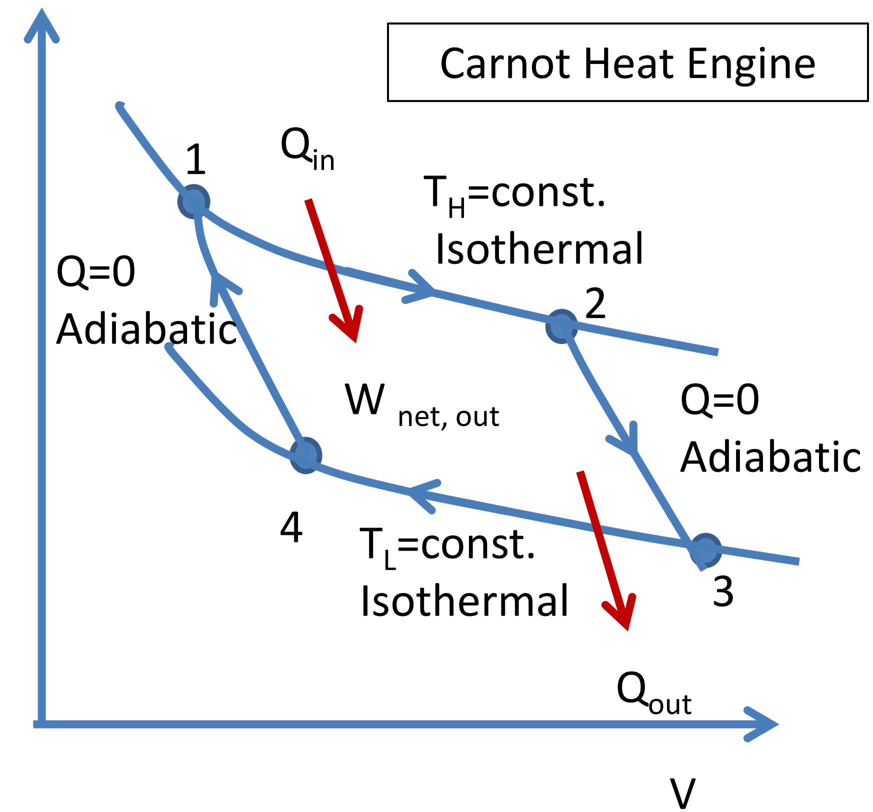


$$\boxed{\lim_{n \to \infty} W = 0} \longleftarrow$$ **REVERSIBLE PROCESS**

Carnot Cycle

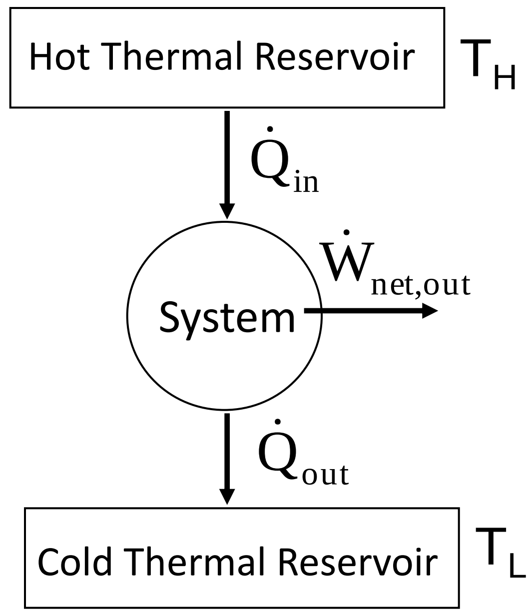
- Reversible cycles are most efficient
- Provides upper limits on the performance of real cycles
- Carnot cycle is the best known reversible cycle (theoretical, idealized process)





Reversed Carnot Cycle= Carnot Refrigeration

Derivation of Entropy

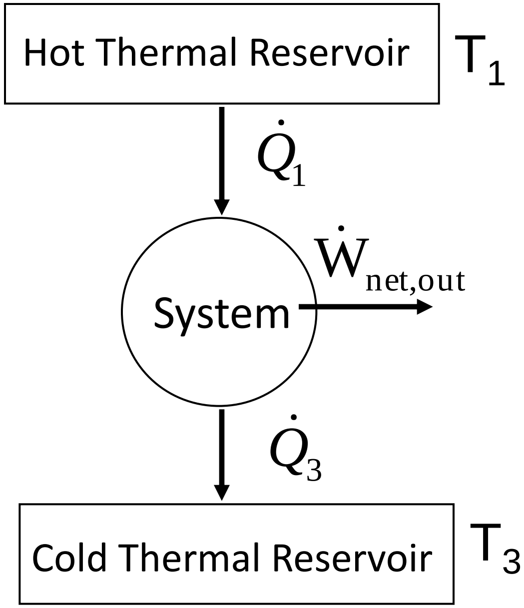


$$\eta_{Th} = \frac{W_{out} - W_{in}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

$$\eta = f\left(T_H, T_L\right)$$

$$\frac{Q_{out}}{Q_{in}} = f\left(T_H, T_L\right)$$

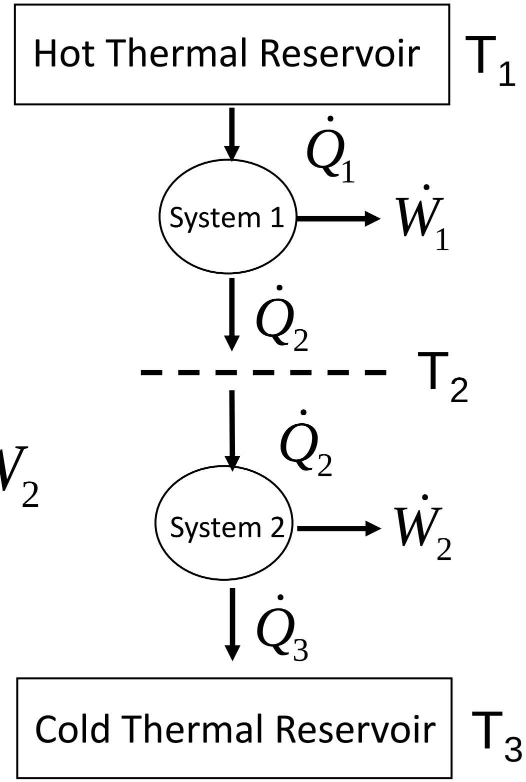
Derivation of Entropy



$$\frac{Q_3}{Q_1} = f\left(T_1, T_3\right)$$

If reversible

$$W_{net} = W_1 + W_2$$



$$\frac{Q_2}{Q_1} = f\left(T_1, T_2\right)$$

$$\frac{Q_3}{Q_2} = f\left(T_2, T_3\right)$$

$$\frac{Q_3}{Q_1} = \frac{Q_2}{Q_1} \cdot \frac{Q_3}{Q_2} \qquad f\left(T_1, T_3\right) = f\left(T_1, T_2\right) \cdot f\left(T_2, T_3\right)$$

$$f\left(T_1, T_2\right) = \frac{g\left(T_2\right)}{g\left(T_1\right)} \qquad f\left(T_2, T_3\right) = \frac{g\left(T_3\right)}{g\left(T_2\right)}$$

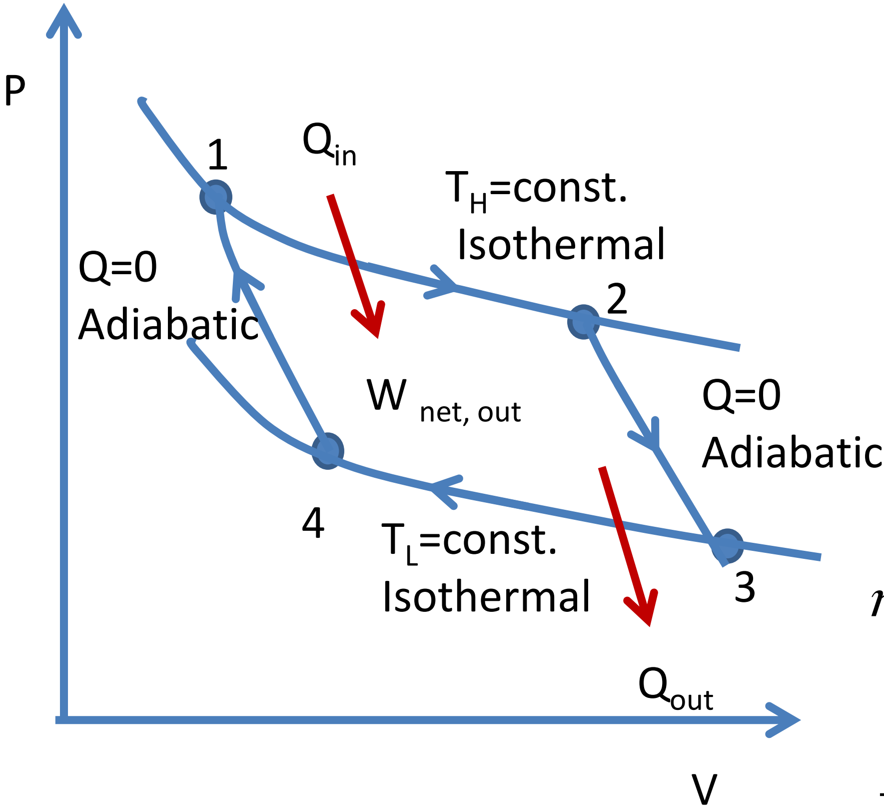
$$f\left(T_1, T_3\right) = \frac{g\left(T_3\right)}{g\left(T_1\right)}$$

$g\left(T\right) = T$ If T is <u>absolute</u> T

$$\left(\frac{Q_{out}}{Q_{in}}\right)_{rev} = \frac{T_L}{T_H}$$

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

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

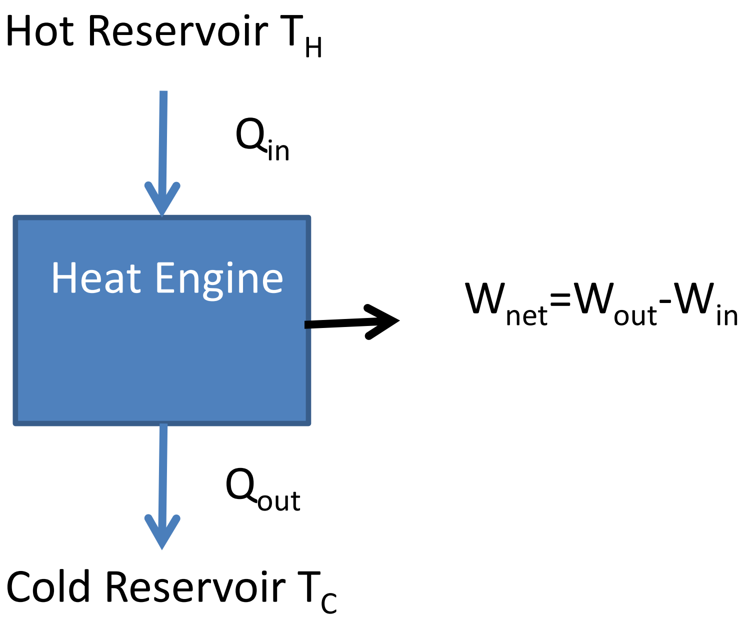
$$\eta_{Th} = \frac{W_{out} - W_{in}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{T_L}{T_H}$$

$$\frac{Q_{in}}{T_H} = \frac{Q_{out}}{T_L} \qquad \frac{Q}{T} = S$$

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

$$dS = S_{in} - S_{out} = 0$$

Reversible Heat Engine Cycles determine the Maximum Efficiency



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

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

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

Irreversible Cycle

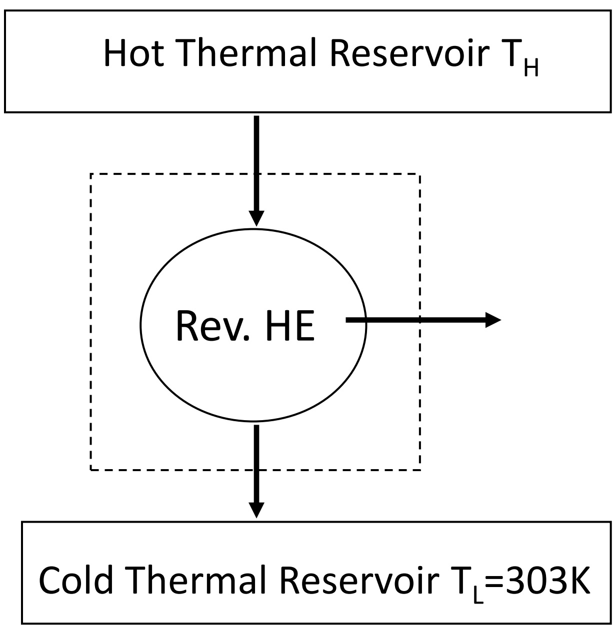
$$\eta_{irreversible} = \frac{W_{net,out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

Reversible Cycle

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

How do we increase η ?

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



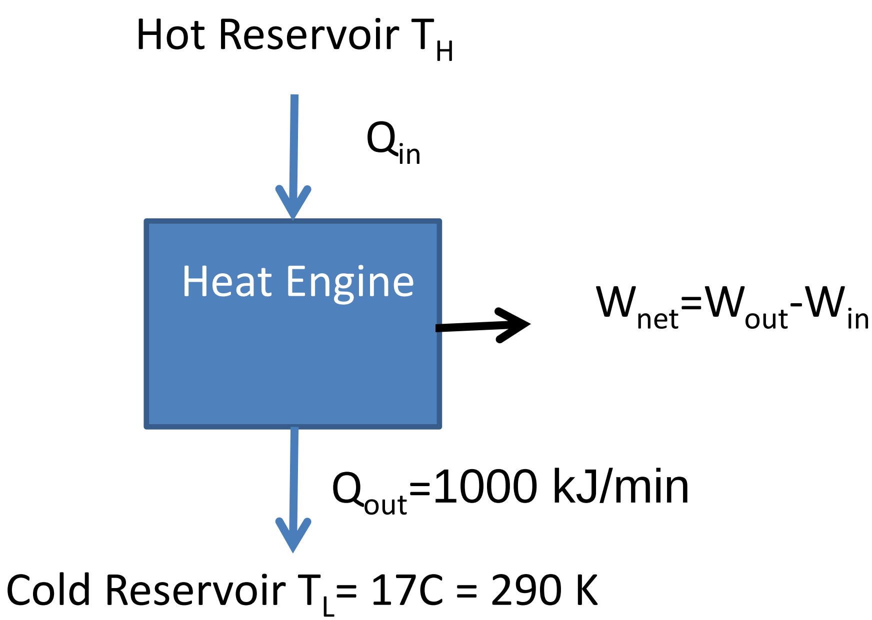
T_H	$\eta_{reversible}$
925K	67.2%
700K	56.7%
350K	13.4%

Quality of energy

The thermal efficiency of an internally reversible heat engine is 60%. A cooling pond receives 1000 kJ/min of heat transfer from the working fluid at 17^{o}C.

Determine

(a) the power output of the engine in kW and
(b) the temperature of the fluid during heat addition, in ^{o}C.
(c) An actual heat engine operating between the same temperatures has a work output which is ½ of the internally reversible engine. Assuming the same heat input, find the rate of heat rejection.

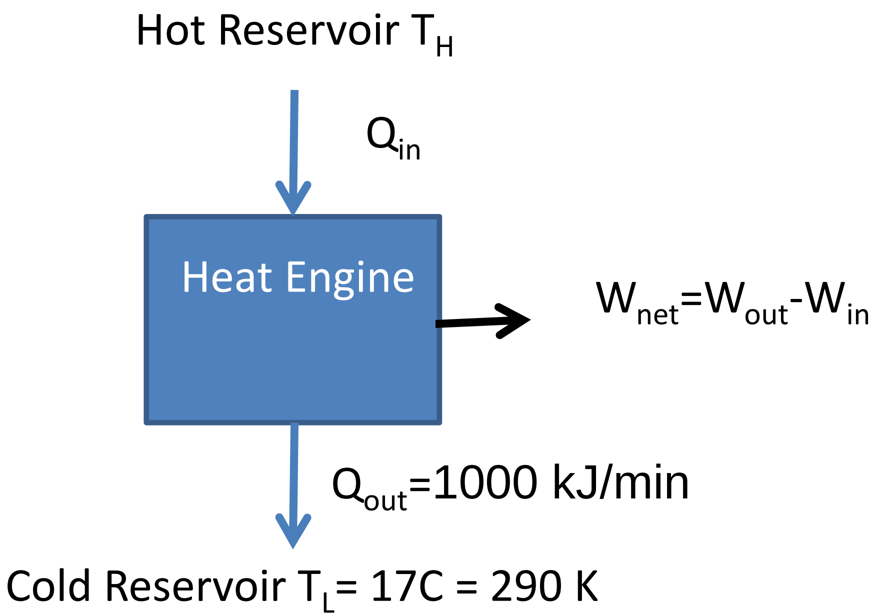


$$\eta_{Th} = 0.60 = \frac{W_{out} - W_{in}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

$$\eta_{Th} = 0.60 = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{1000 kJ / \min}{Q_{in}}$$

$$Q_{in} = 2500 kJ / \min$$

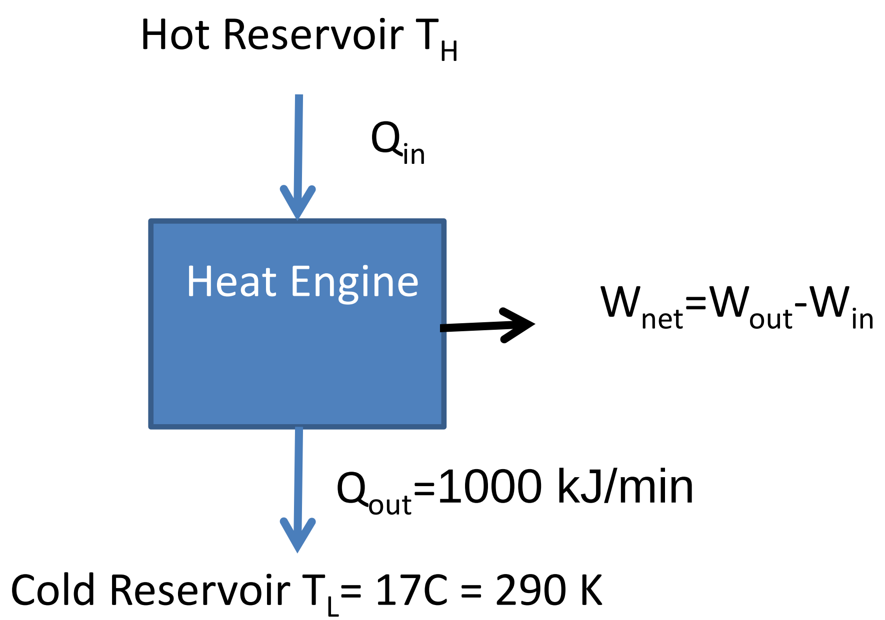
$$W_{out} = Q_{in} - Q_{out} = 2500 - 1000 = 1500 kJ / \min = 25 kW$$



$$\eta_{Th} = \eta_{reversible} = 0.60 = 1 - \frac{T_L}{T_H}$$

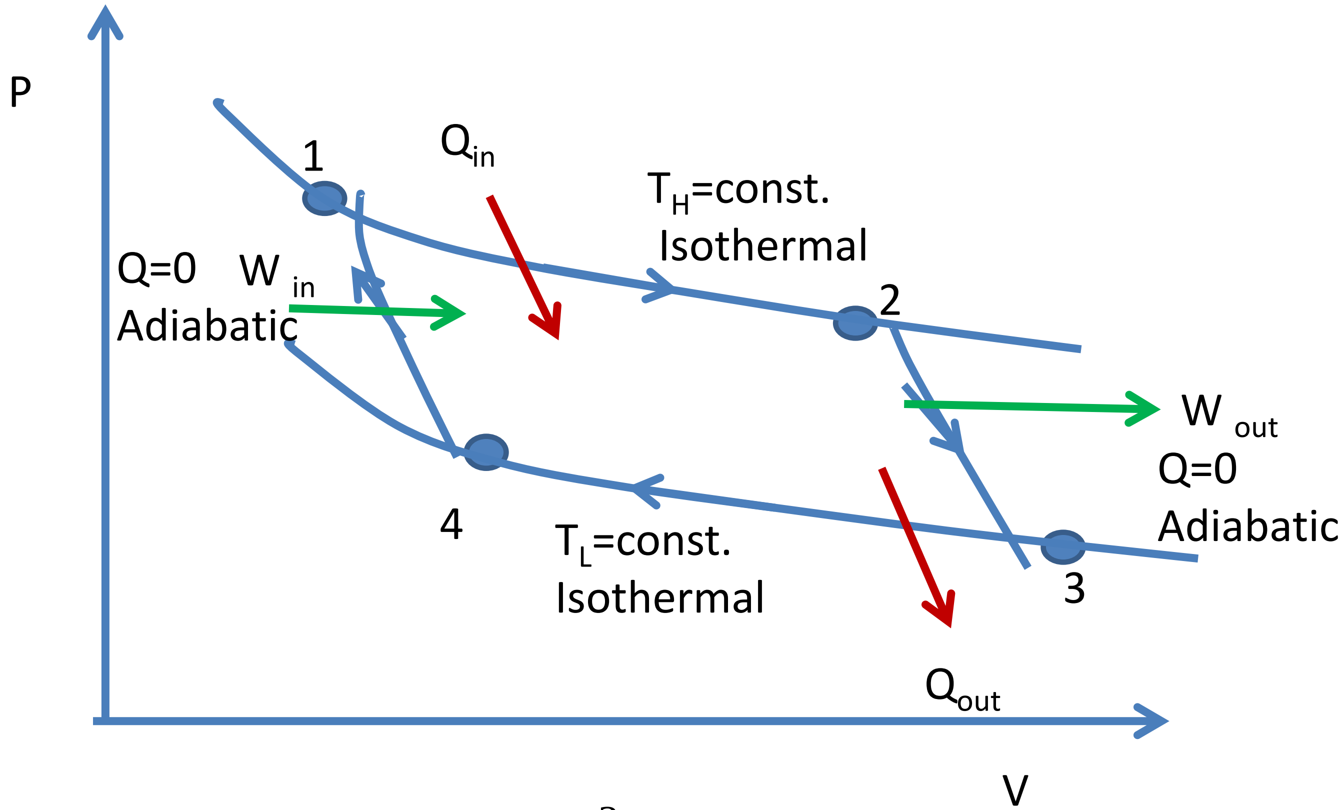
$$0.60 = 1 - \frac{290K}{T_H}$$

$$T_H = 725K = 452\,^0C$$

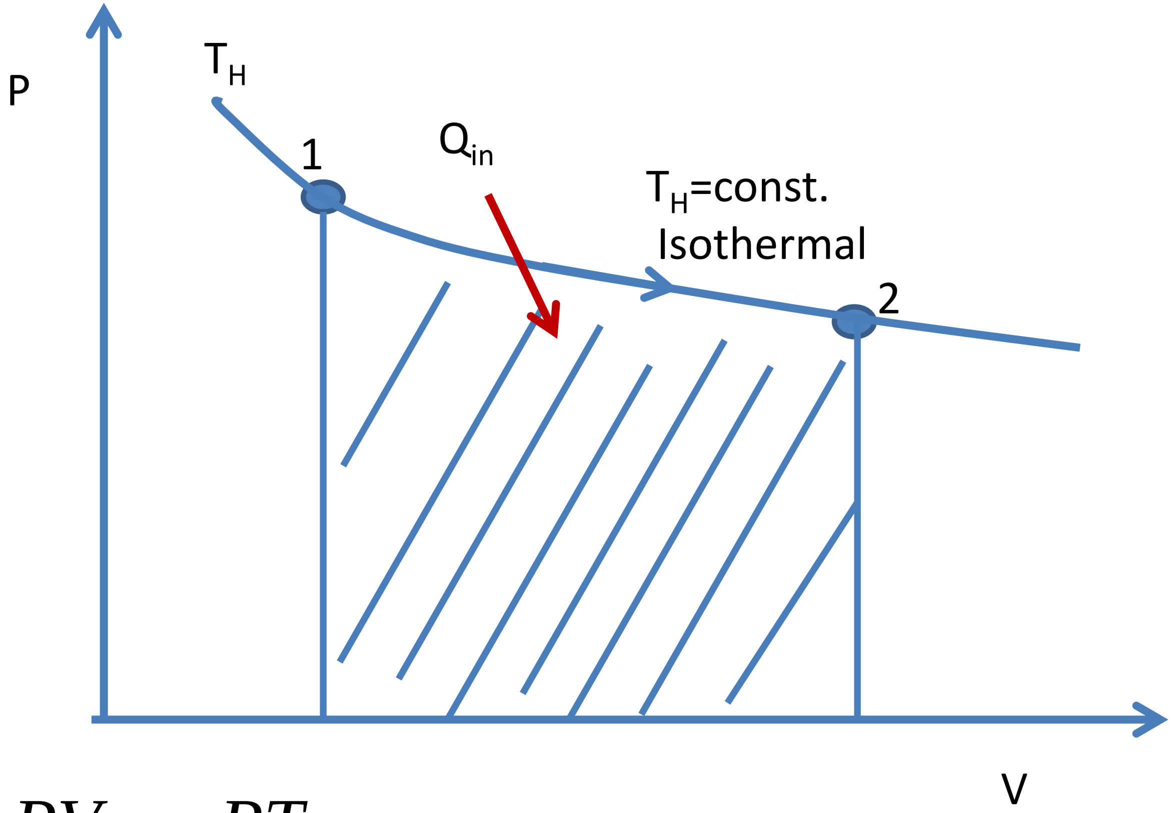


$$W_{out} = \frac{1500kJ/\min}{2} = 750kJ/\min = Q_{in} - Q_{out} = 2500 - Q_{out}$$

$$Q_{out} = 1750kJ/\min = 29kW$$



$$PV = \frac{N}{m^2}\frac{m^3}{1} = Nm = J$$



$$\Delta U = Q_{1-2} - W_{1-2}$$

$$\Delta U = 0 = Q_{1-2} - W_{1-2}$$

$$Q_{1-2} = W_{1-2}$$

$$W_{1-2} = \int_{V1}^{V2} P dV$$

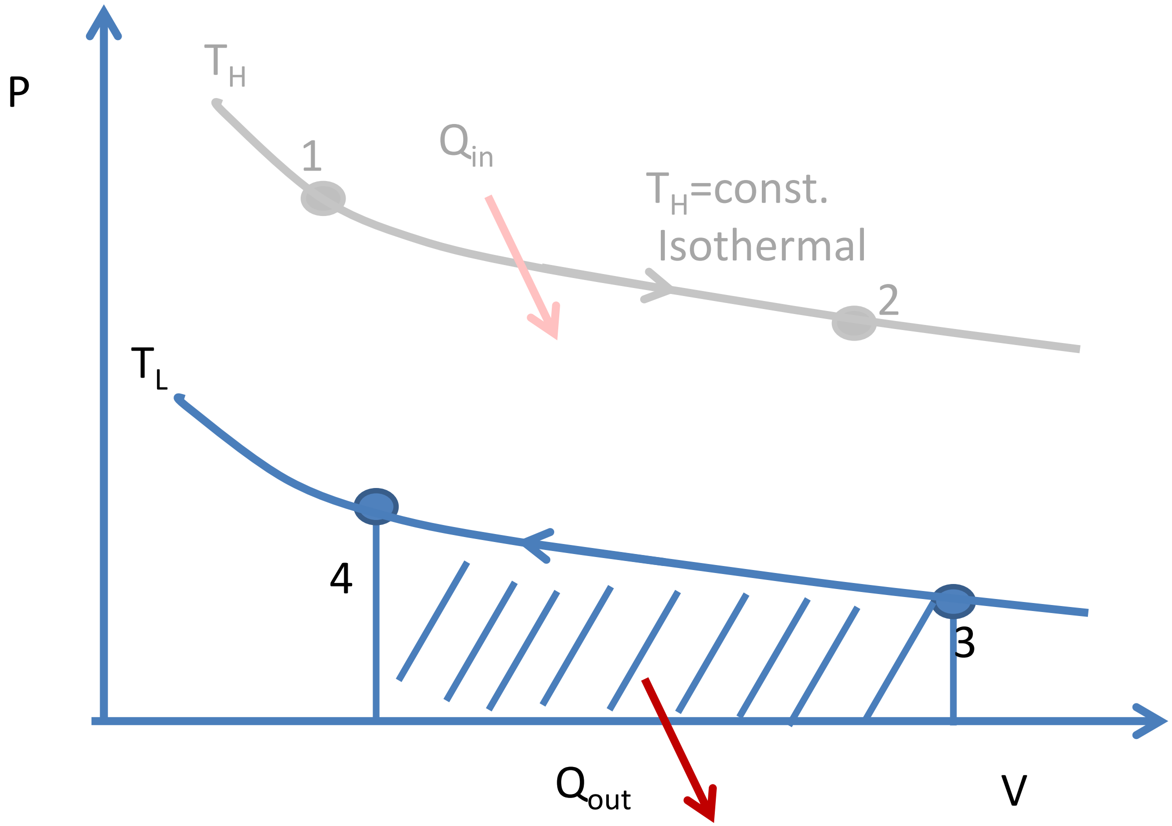
$$Q_{1-2} = nRT \int_{V1}^{V2} \frac{1}{V} dV$$

$$PV = nRT$$

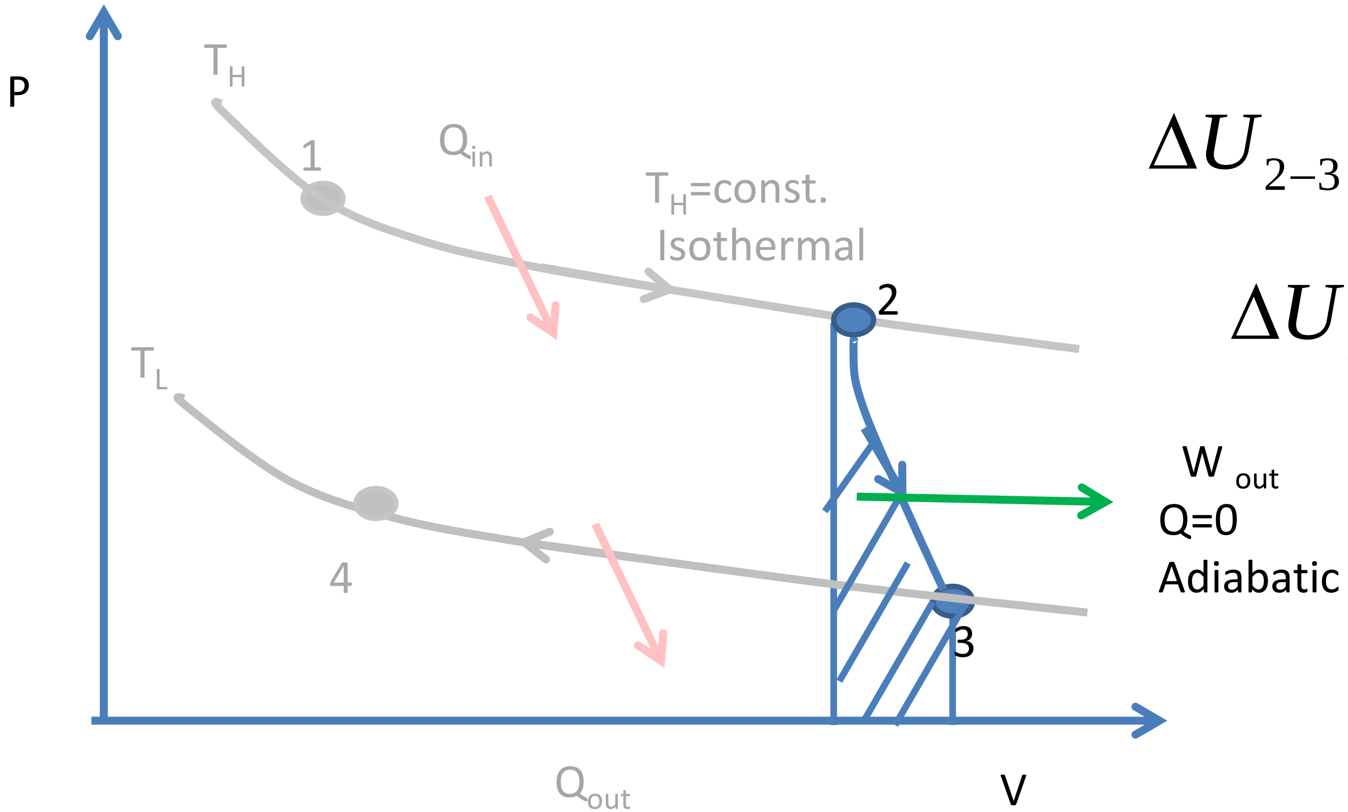
$$P = \frac{1}{V} nRT$$

$$P = C \frac{1}{V}$$

$$Q_{1-2} = Q_{in} = nRT_H \left[\ln V\right]_{V1}^{V2} = nRT_H \ln\left(\frac{V_2}{V_1}\right)$$



$$Q_{3-4} = Q_{out} = nRT_L \left[\ln V\right]_{V3}^{V4} = nRT_L \ln\left(\frac{V_4}{V_3}\right)$$



$$\Delta U_{2-3} = Q_{2-3} - W_{2-3}$$

$$\Delta U_{2-3} = -W_{2-3}$$

$$-W_{2-3} = \Delta U_{2-3} = \int_{T_H}^{T_L} nC_p dT \approx nC_p(T_L - T_H)$$

$$-W_{4-1} = \Delta U_{4-1} = \int_{T_L}^{T_H} nC_p dT \approx nC_p(T_H - T_L)$$

Whole Cycle

$$W_{net} = -nRT_H \ln\left(\frac{V_2}{V_1}\right) + \cancel{nC_p(T_L - T_H)} - nRT_H \ln\left(\frac{V_4}{V_3}\right) + \cancel{nC_p(T_H - T_L)}$$

$$W_{net} = -nRT_H \ln\left(\frac{V_2}{V_1}\right) - nRT_H \ln\left(\frac{V_4}{V_3}\right)$$