ME-251: Thermodynamics and energetics I
2^{nd} Law II

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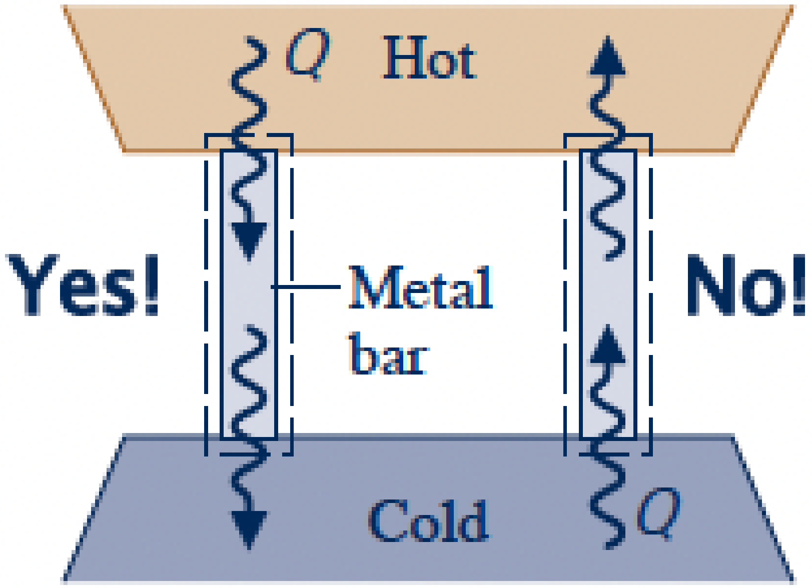
Photo Credit: Trougnouf

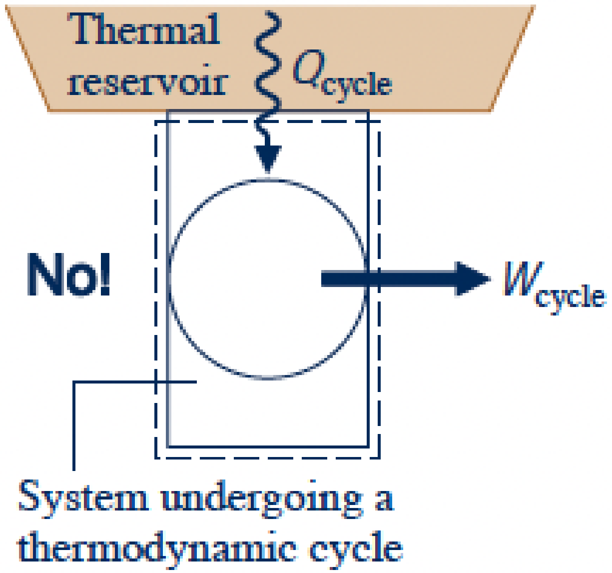
2nd Law of Thermodynamics



Clausius statement. 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.

It is possible for a system to transfer energy by heat from a cooler body to a hotter body (refrigerators, heat pumps, …) but there must be some other effects accomplishing this

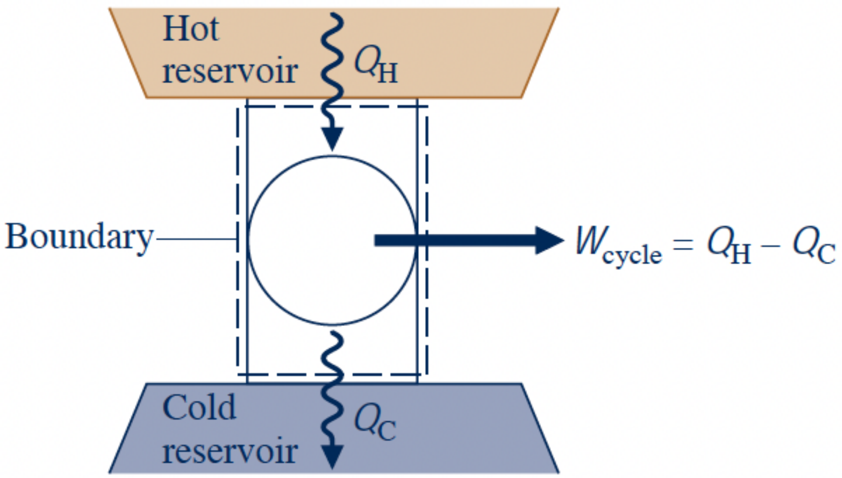
2nd Law of Thermodynamics



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

A **thermal reservoir** is a special kind of system that always remains at constant temperature even though energy is added or removed by heat transfer.

Carnot Engine

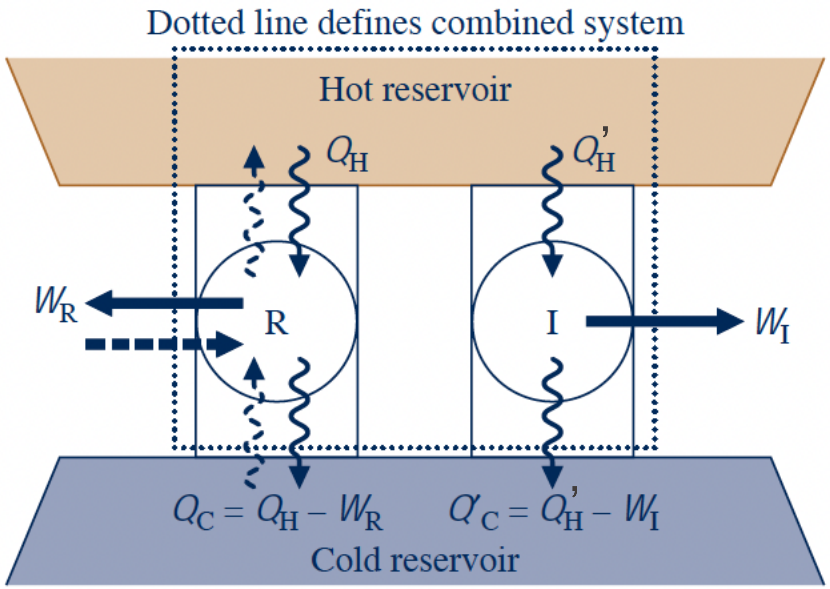


$$\eta = W_{cycle}/Q_H$$

A Carnot engine is any engine that is reversible, runs in a cycle, exchanging heat only with a hot reservoir (source) at temperature T_H and a cold reservoir (sink) at temperature T_C

Carnot's Theorem: No engine operating between two reservoirs (at temperatures T_H and T_C) is more efficient than a Carnot engine operating between them.

Corollary

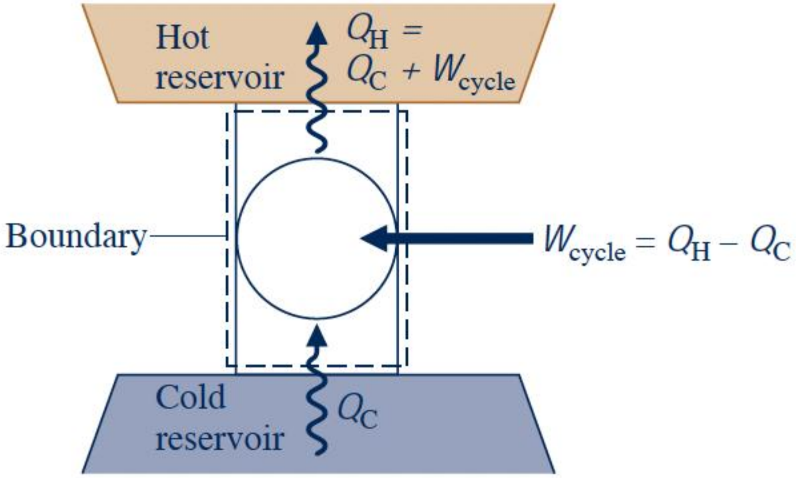


All reversible (Carnot) engines have the same universal efficiency $\eta(T_H, T_C)$

Consider any two Carnot engines with η_1 and η_2 : each can be used to run the other backward

$$\eta_1 \leq \eta_2 \text{ and } \eta_2 \leq \eta_1 \Rightarrow \eta_2 = \eta_1$$

Corollaries of 2nd Law for Refrigeration and Heat Pump Cycles



Refrigeration COP: $\beta = Q_C/W_{cycle}$

Heat pump COP: $\gamma = Q_H/W_{cycle}$

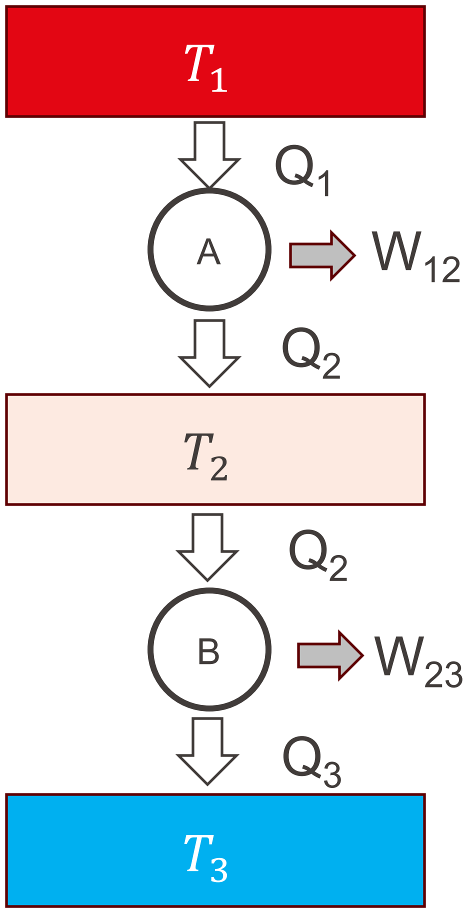
No refrigeration cycle operating between two thermal reservoirs has a higher COP than a reverse Carnot engine

All reversible refrigeration cycle operating between the same two thermal reservoirs have the same COP.

ILOs Today

- Thermodynamic temperature scale
- Carnot efficiency
- Carnot cycle
- Clausius inequality and its relation to entropy
- Evaluation of entropy change

Thermodynamic Temperature Scale

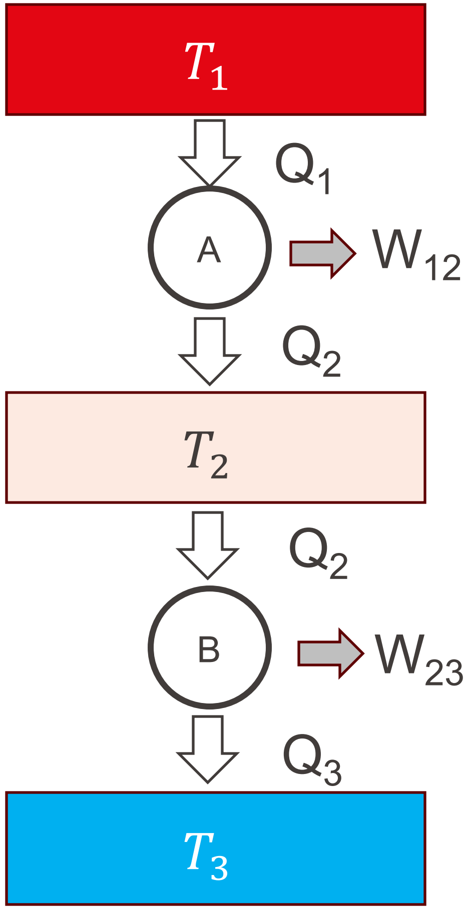


Consider two Carnot engines running in series, one between T_1 and T_2 and another between T_2 and T_3 ($T_1 > T_2 > T_3$)

Heat dumped by the 1st engine is received by the 2nd

Combining the two engines and T_2 reservoir, we have another Carnot engine between T_1 and T_3 with work

Thermodynamic Temperature Scale



Thermodynamic Temperature Scale

A theoretical approach to define temperature through Carnot engines, not practically useful, but independent of substances (conceptually clean)

All thermodynamic temperatures are positive
$\eta_c(T_1, T_2) = 1 - T_2/T_1$ cannot be greater than 1

Carnot Efficiency

Maximum theoretical power cycle efficiency between two thermal reservoirs ($T_H > T_C$)

$$\eta_{max} = \eta_c = 1 - T_C/T_H$$

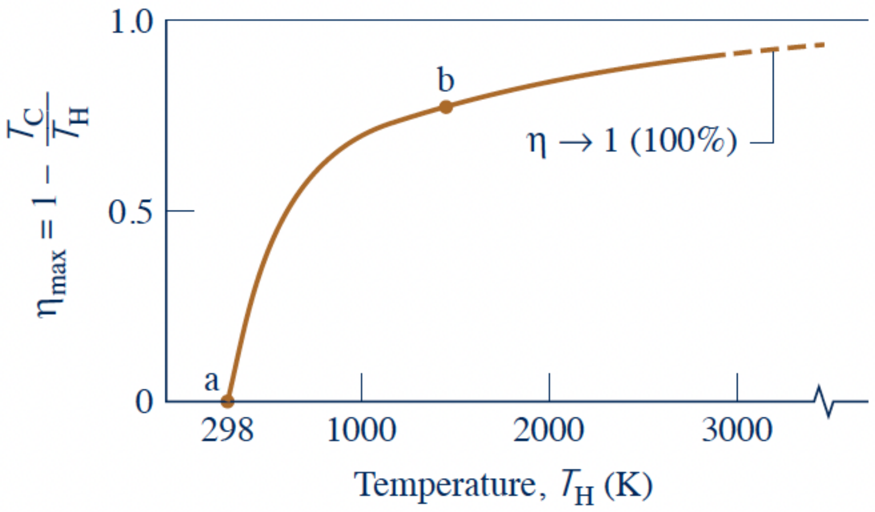


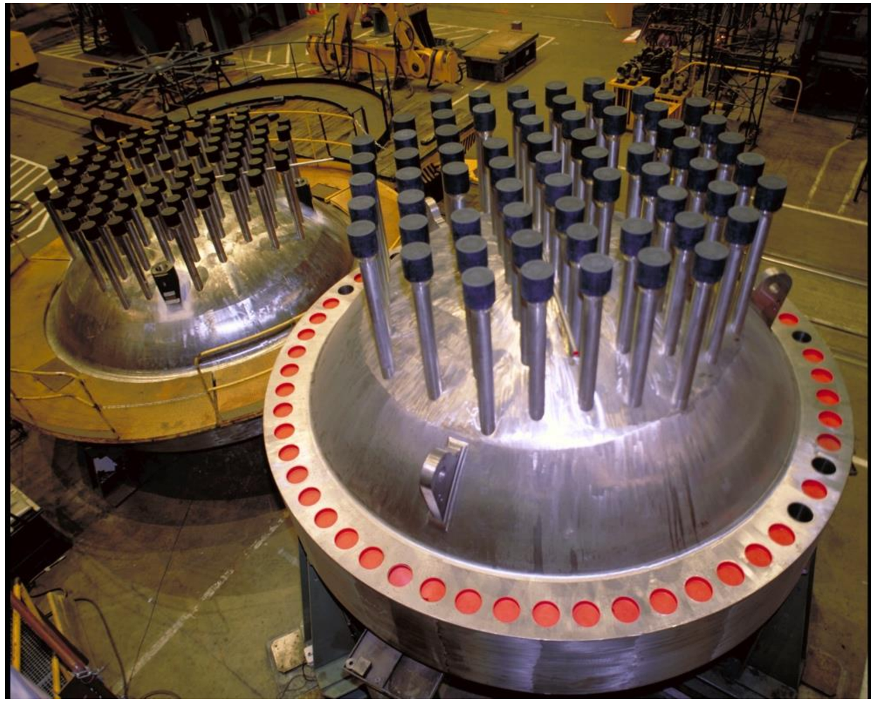
Fig. 5.12 **Carnot efficiency versus T_H, for T_C = 298 K.**

One effective approach to increase the maximum efficiency of power plants is to increase the hot-side temperature

Quest for High Temperature

Credit: Koza1983, CC BY 3.0

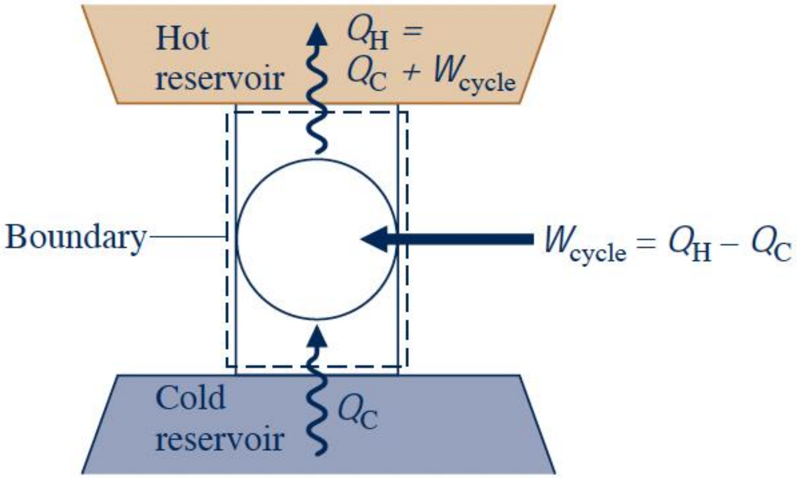
Concentrated solar power plant



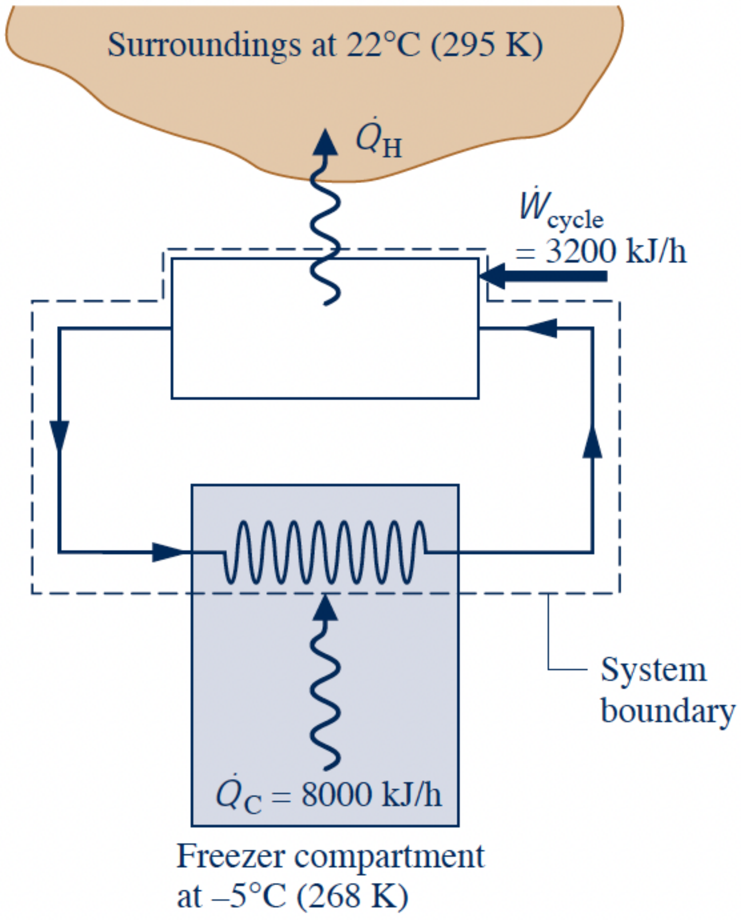
Credit: NRC

Pressurized water nuclear reactor

Refrigeration and Heat Pump Cycles



Moran Example 5.2



A refrigerator maintains a freezer compartment at -5 °C while the ambient temperature is at 22 °C

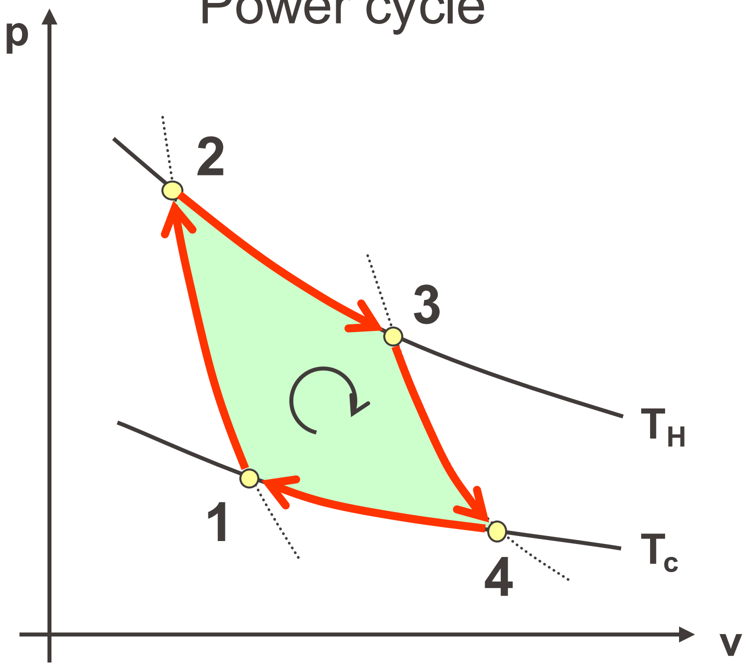
The heat transfer rate from the refrigerated space and the power input are known

Calculate the theoretical maximum COP given the temperature conditions and the actual COP

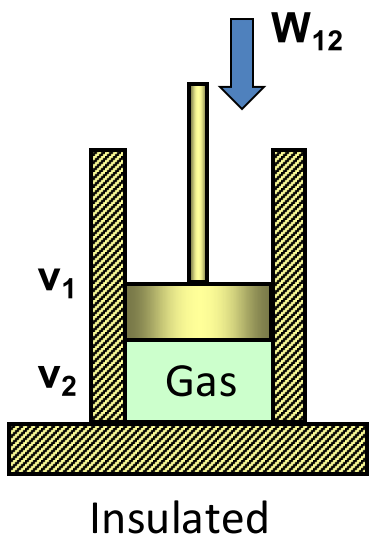
Carnot Cycle

A reversible cycle that undergoes four reversible processes: two adiabatic processes alternated with two isothermal processes.

Power cycle

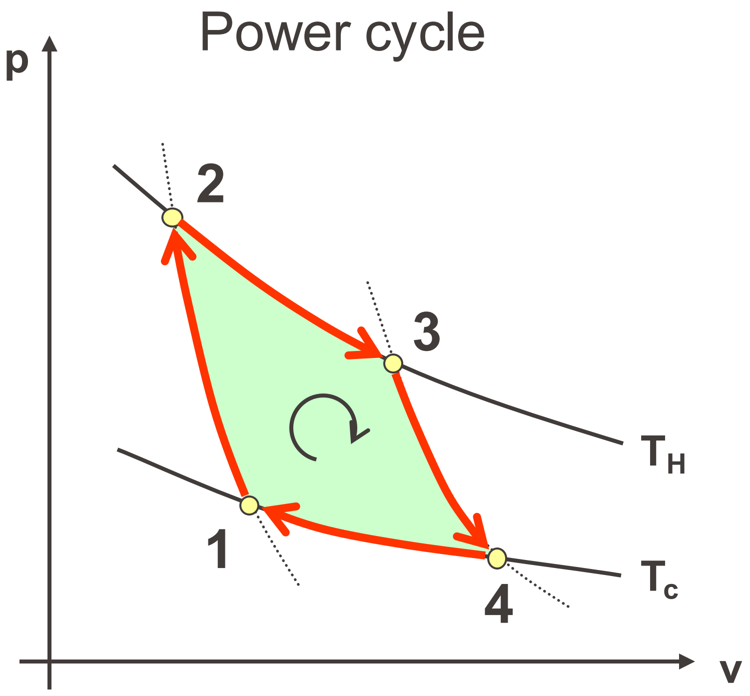


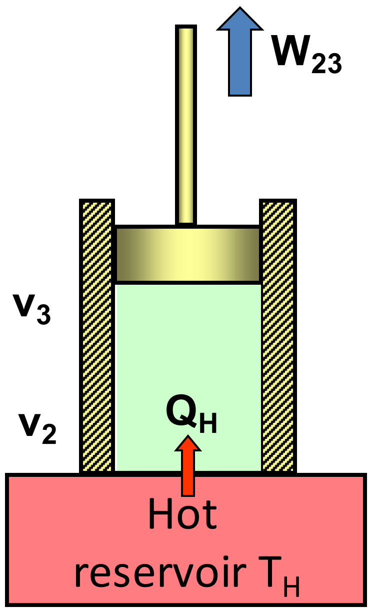
1-2 adiabatic compression



Carnot Cycle

2-3 isothermal expansion receiving heat

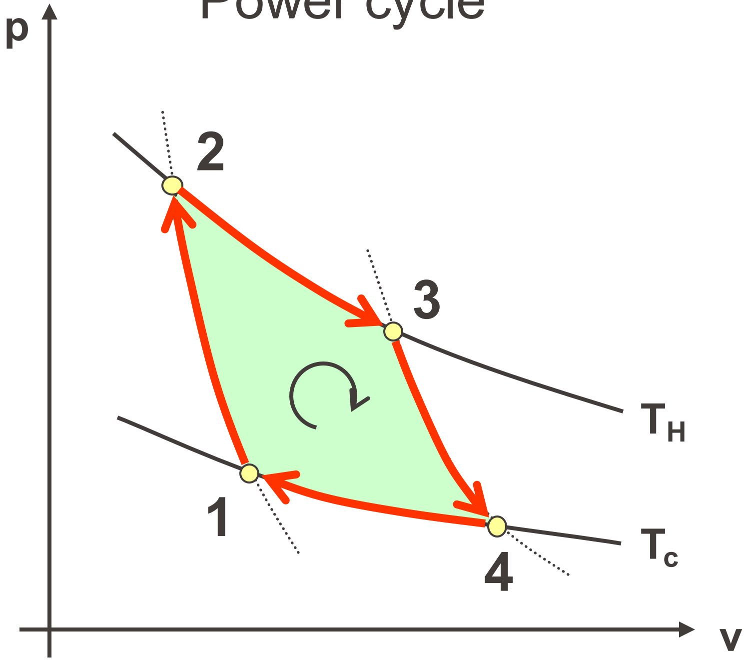


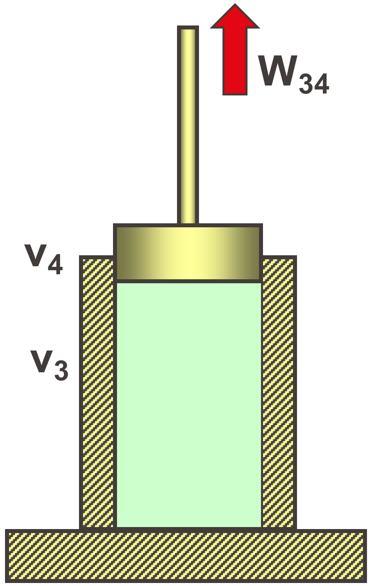


Carnot Cycle

3-4 adiabatic expansion

Power cycle

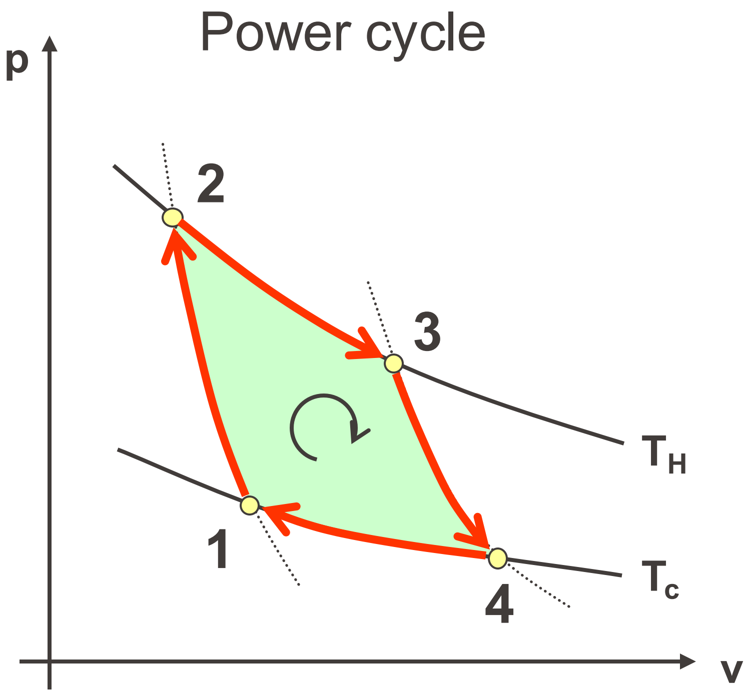


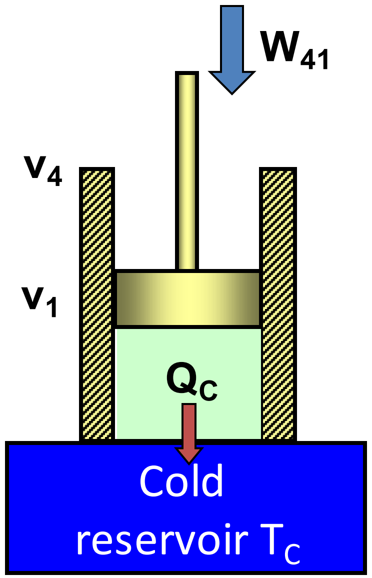


Insulated

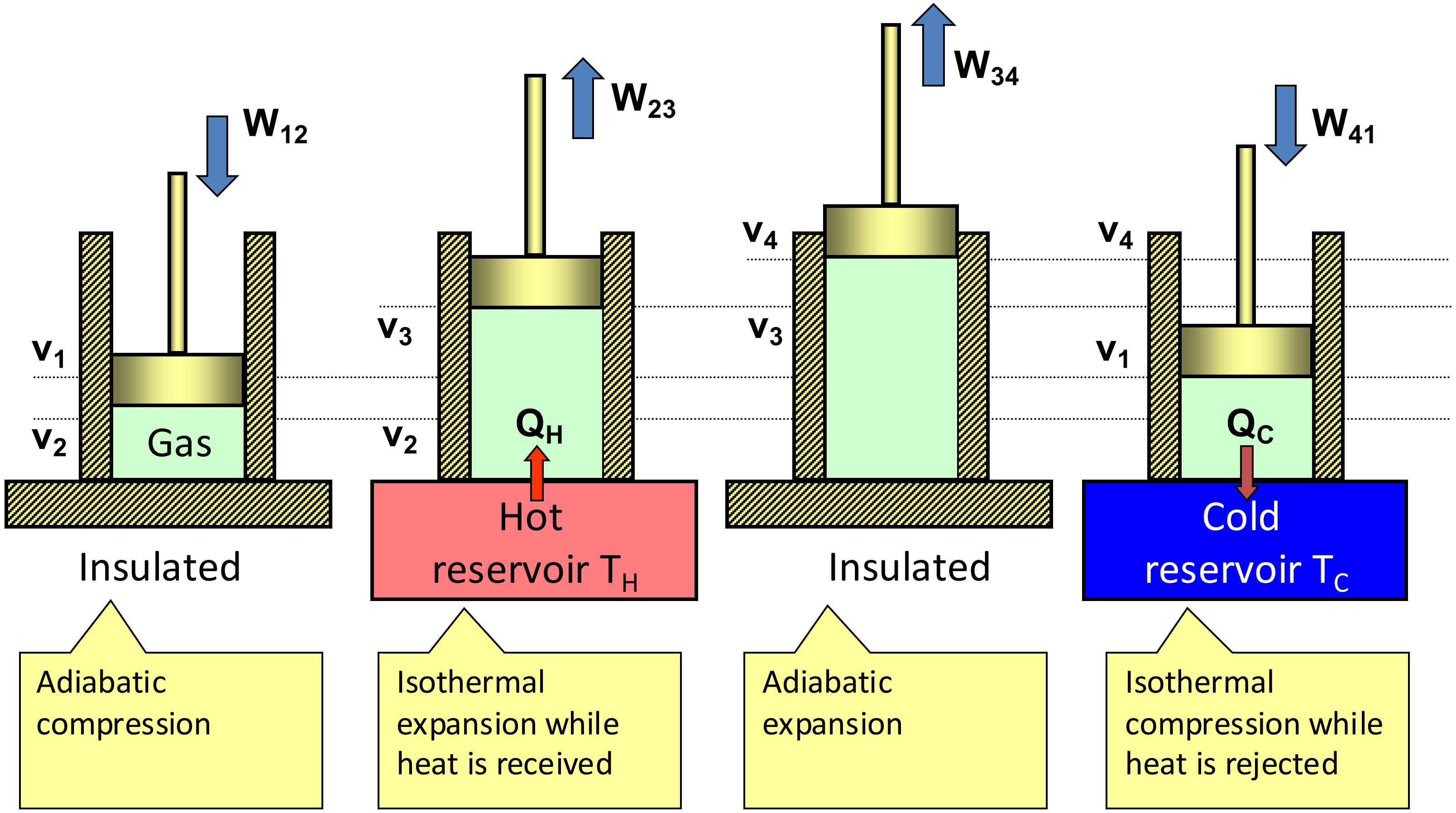
Carnot Cycle

4-1 Isothermal compression discharging heat



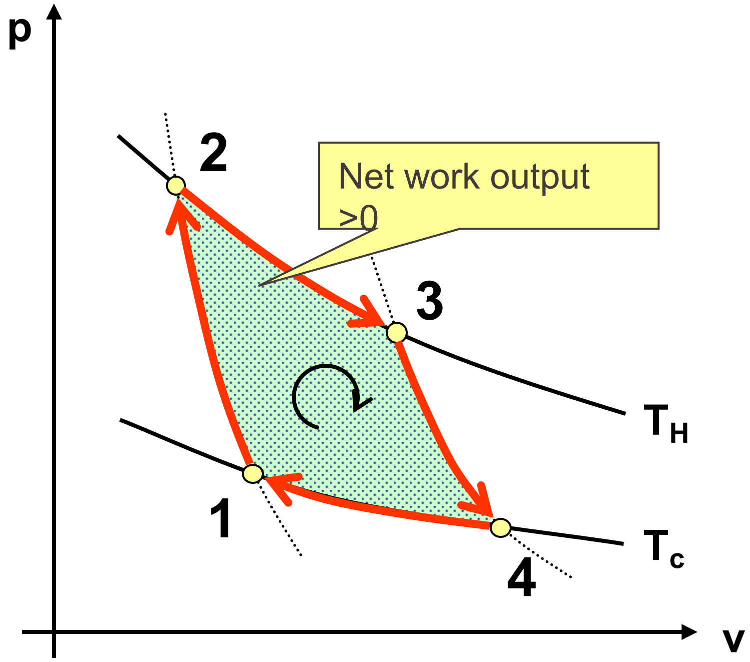


Carnot Power Cycle

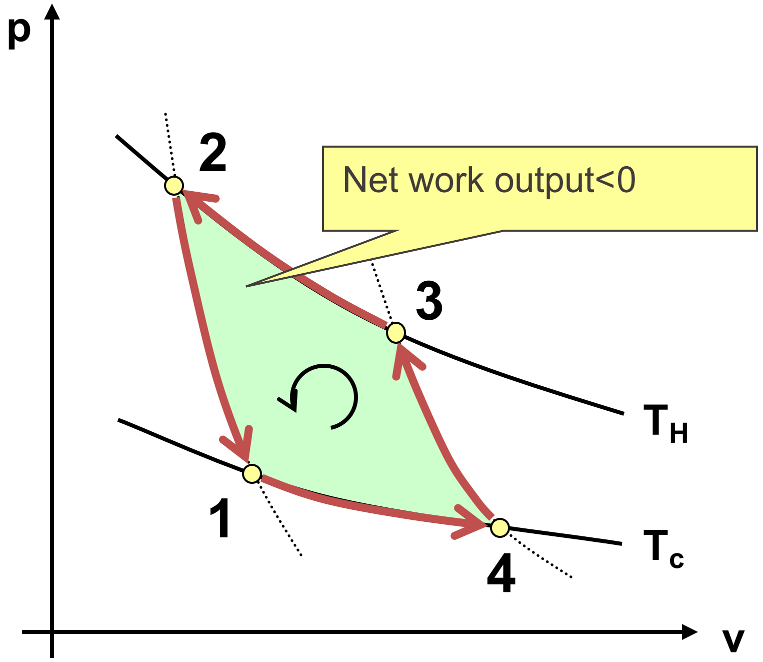


Carnot Cycle (Original and Reversed)

Power Cycle



Refrigeration cycle

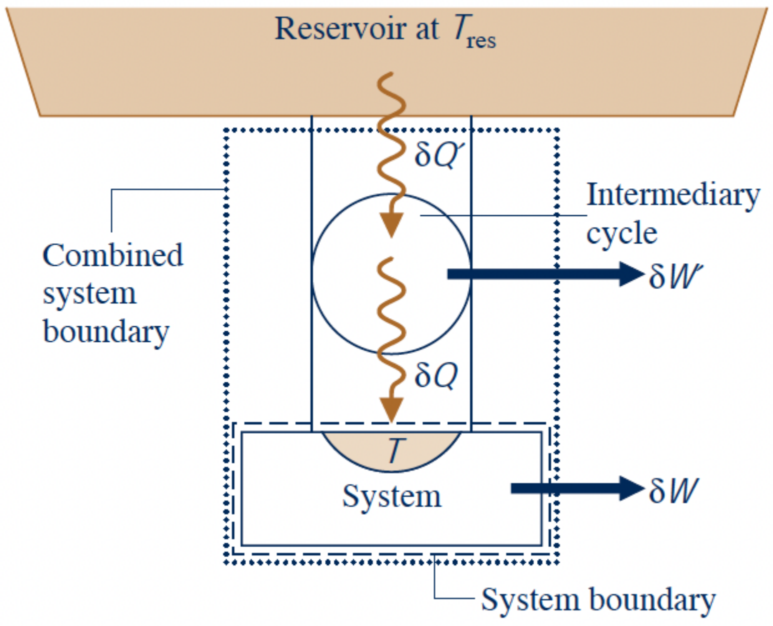


Clausius Inequality

For any thermodynamic cycle (reversible or not), $\oint \frac{\delta Q}{T} \leq 0$

where δQ represent the incremental heat supplied to the system at temperature T for each small time step

Clausius Inequality (Proof)

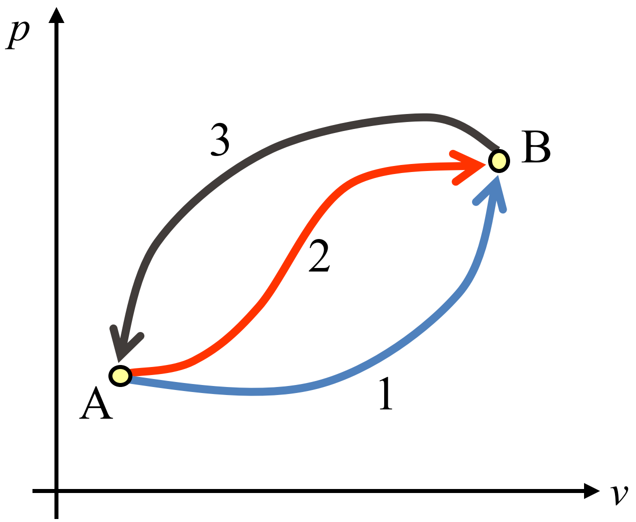


Imagine at each time step, δQ is discharged to the system is from a Carnot engine (operating between T_{res} and system temperature T at any given time)

When the cycle is over, consider the combined system including the Carnot engine and the original system

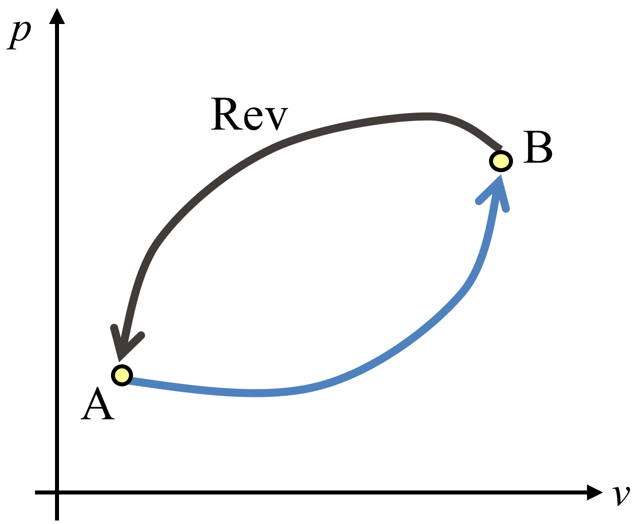
Consequence of Clausius Theorem

For a reversible cycle $$\oint \frac{\delta Q_{rev}}{T} \leq 0$$



Entropy

Construct a state function S



More on Entropy

Entropy is an extensive property: S [J/K]

Specific entropy: s [J/kg/K] intensive

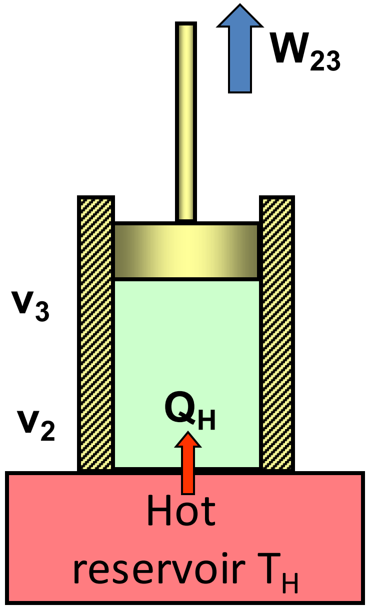
In statistical thermodynamics, entropy measures the uncertainty of a system

Boltzmann entropy formula $S = k_B \ln \boldsymbol{W}$

W represents the number of ways atoms/molecules in a system can be arranged

E.g., for single-species gas system, we care about how gas molecules are distributed in space and how their velocities are distributed

Example



Isothermal expansion receiving heat

Uncertainty about the velocity is characterized by the temperature, which stays the same

Uncertainty about the location is characterized by the volume.

Larger volume -> higher uncertainty in location -> higher S

Thermodynamic Relation

Consider a differential reversible transformation from a certain state

If the only form of work is expansion/compression, ignoring kinetic and potential energy

Entropy Change

Incompressible substance

Entropy Change

Ideal gas

T-s diagrams

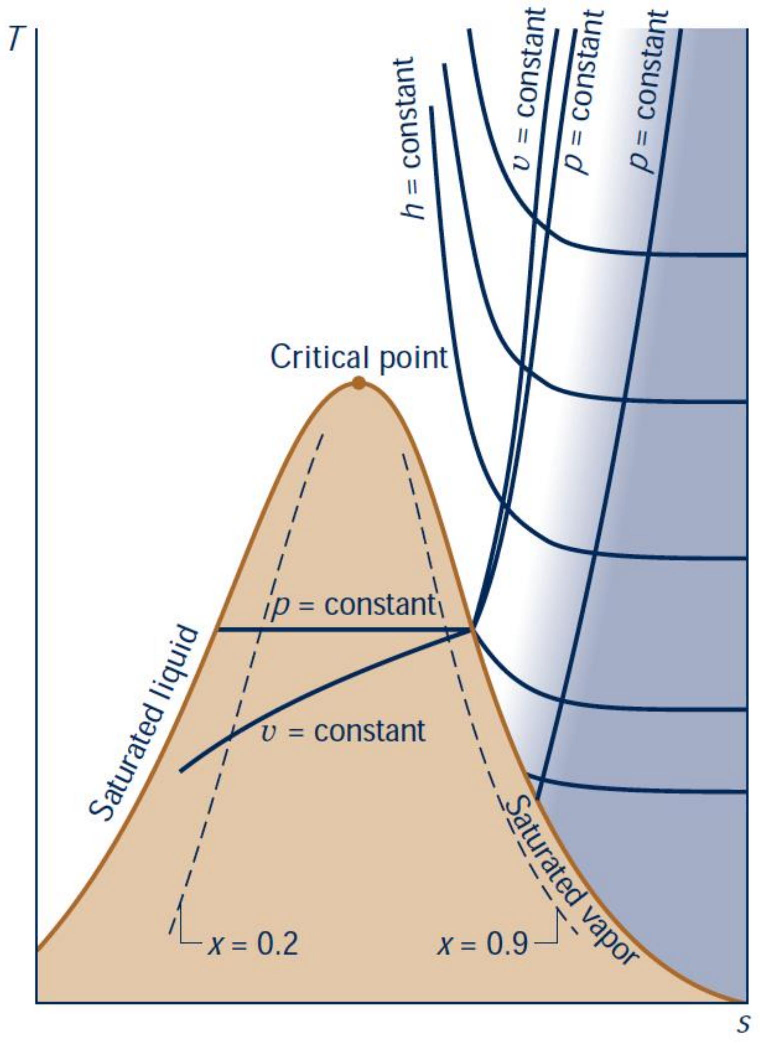


Fig. 6.2 Temperature–entropy diagram.

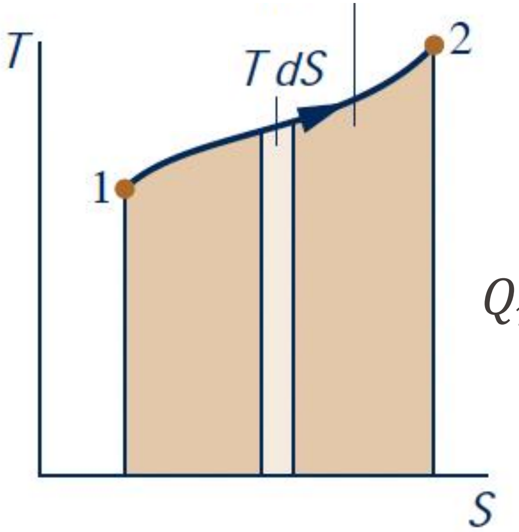
Ideal gas

$$ds = c_v(T) \cdot \frac{dT}{T} + R \cdot \frac{dv}{v}$$

$$ds = c_p(T) \cdot \frac{dT}{T} - R \cdot \frac{dp}{p}$$

Area Representation of Heat Transfer

$$dS = \frac{\delta Q_{rev}}{T} \Rightarrow \delta Q_{rev} = TdS$$

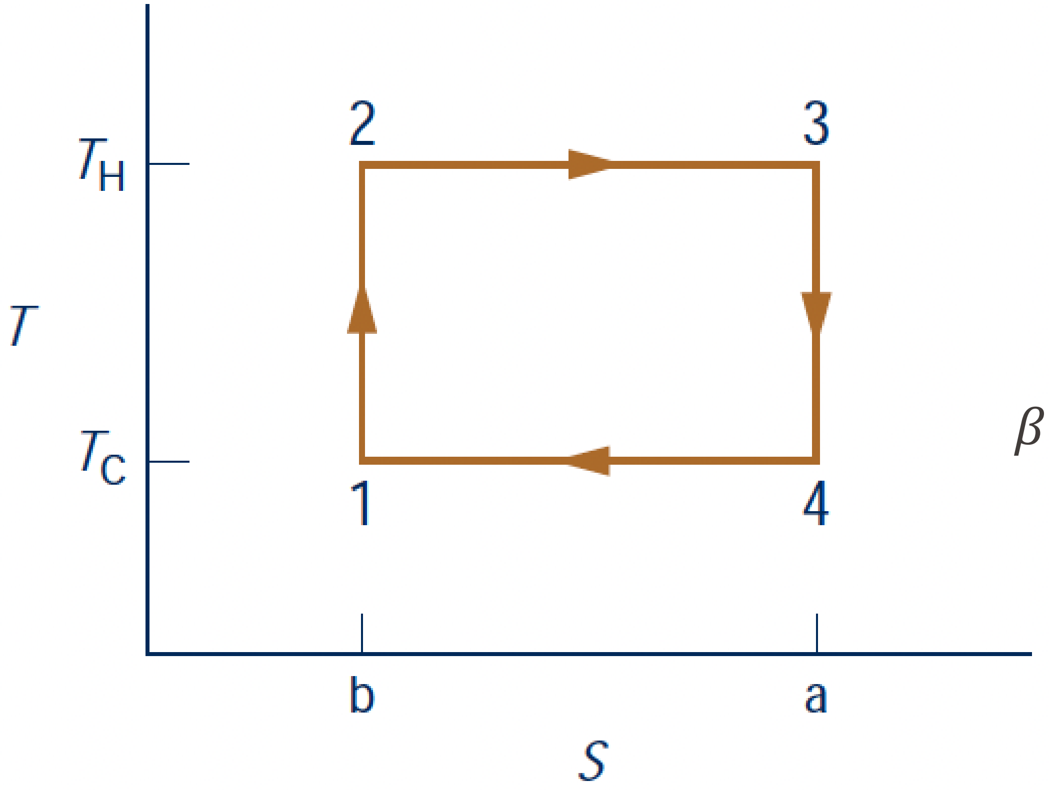


$$Q_{rev} = \int_1^2 TdS$$

Temperature must be in Kelvin

Area only represents the reversible heat transfer

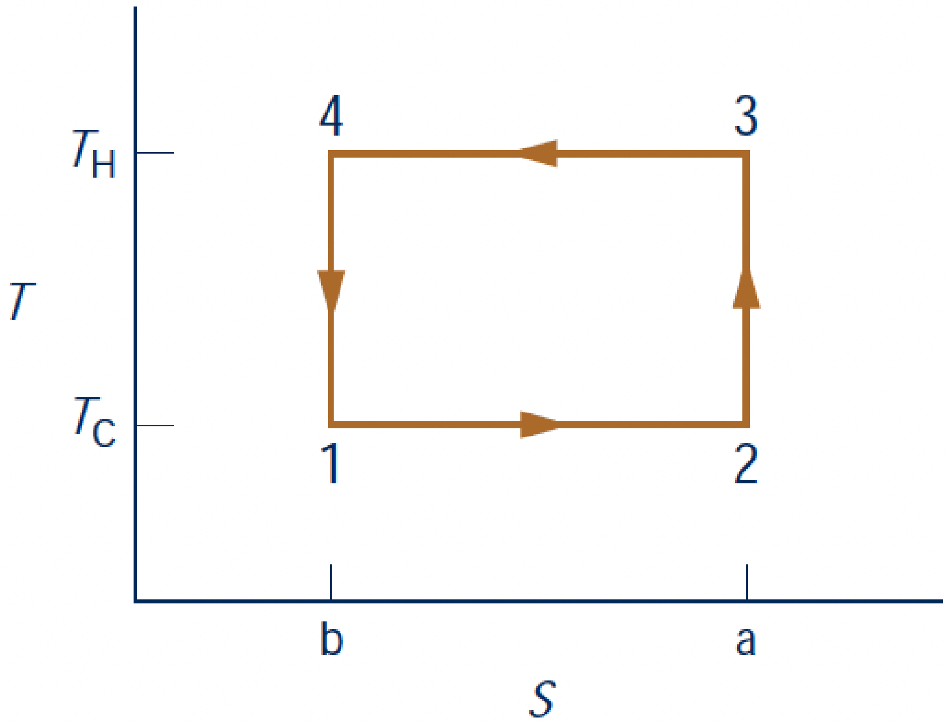
Carnot Cycle



Power cycle

$$\beta = \frac{W_{cycle}}{Q_{23}} = \frac{Q_{23} - Q_{14}}{Q_{23}} = \frac{\text{area } 1-2-3-4-1}{\text{area } 2-3-\text{a}-b-2}$$

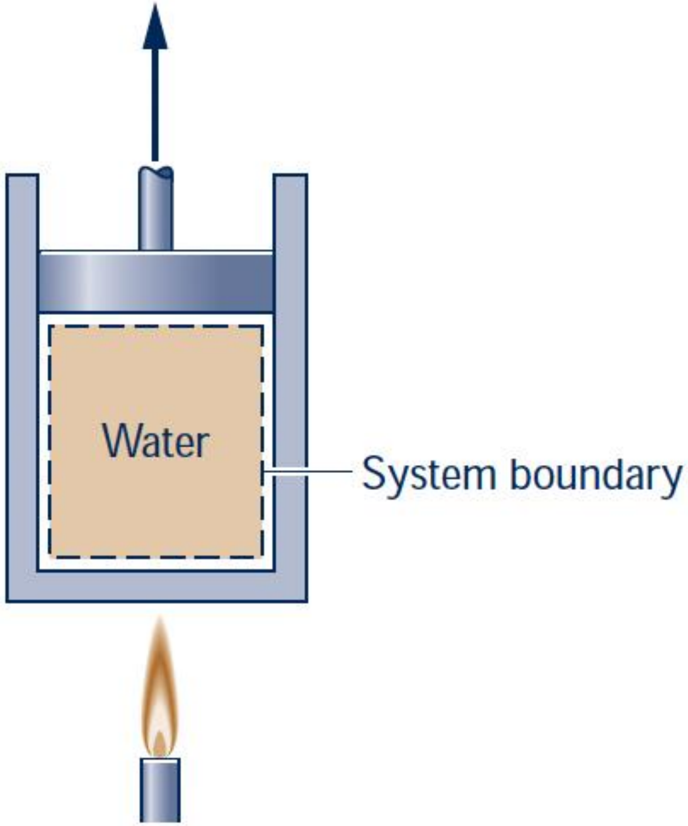
Carnot Cycle



Refrigeration cycle

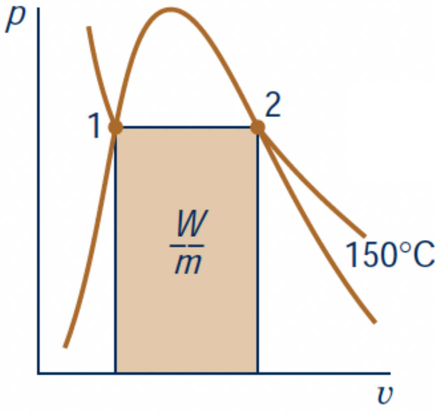
COP $\beta = \dfrac{Q_{12}}{W_{cycle}} = \dfrac{\text{area } 1-2-a-b-1}{\text{area } 1-2-3-4-1}$

Moran Example 6.1



Water contained in a piston-cylinder assembly undergoes a reversible process at 150 °C from saturated liquid to water

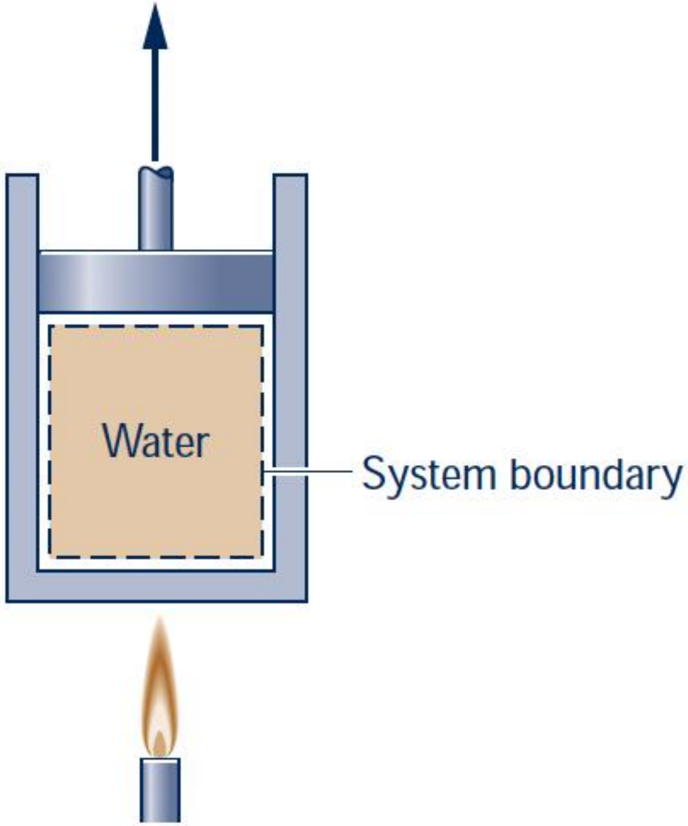
Determine the work and heat transfer per unit mass.



Pressure stays at the saturation pressure at 150 °C

$$\frac{W}{m} = \int_1^2 p dv = p(v_2 - v_1)$$

Moran Example 6.1



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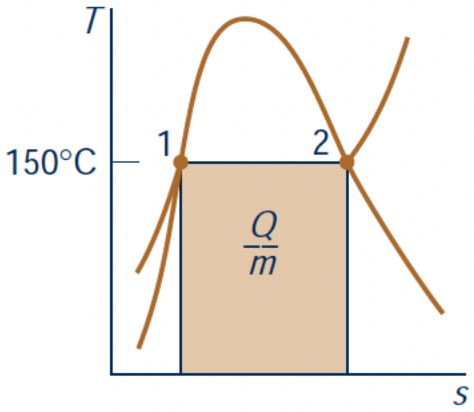

$$\frac{Q_{rev}}{m} = \int_1^2 T ds = T(s_2 - s_1)$$