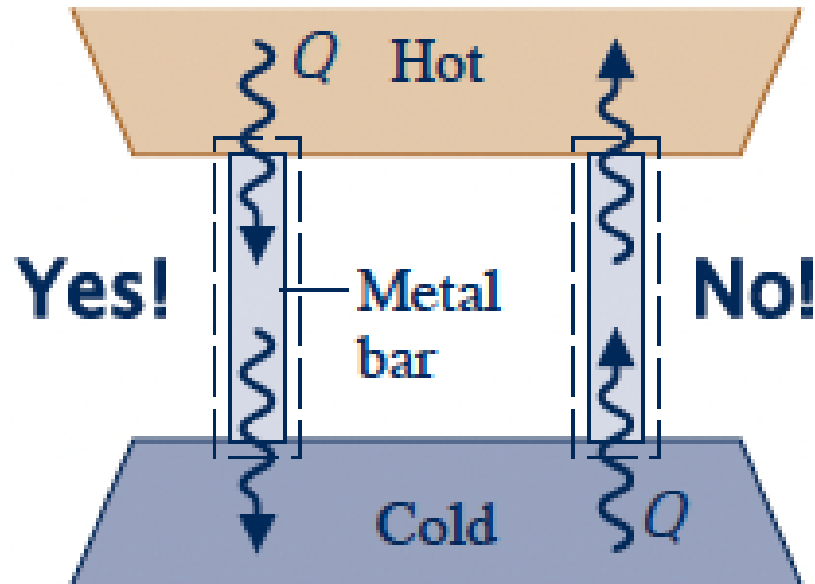


ME-251: Thermodynamics and energetics I 2nd Law II

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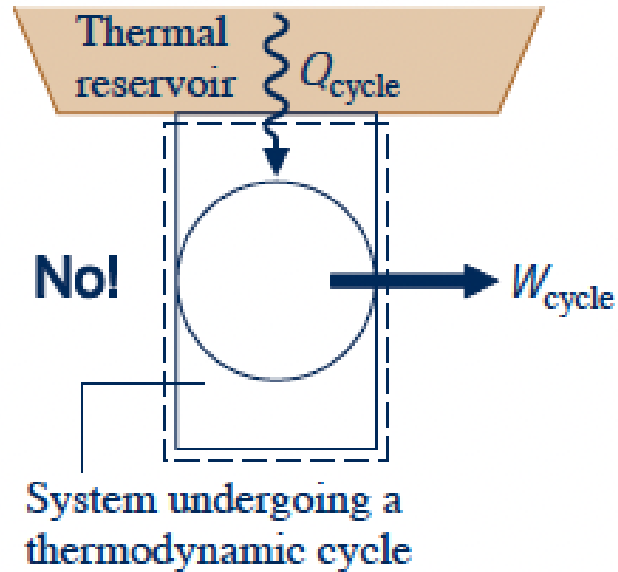
2025 Fall Semester

Photo Credit: Trougnouf



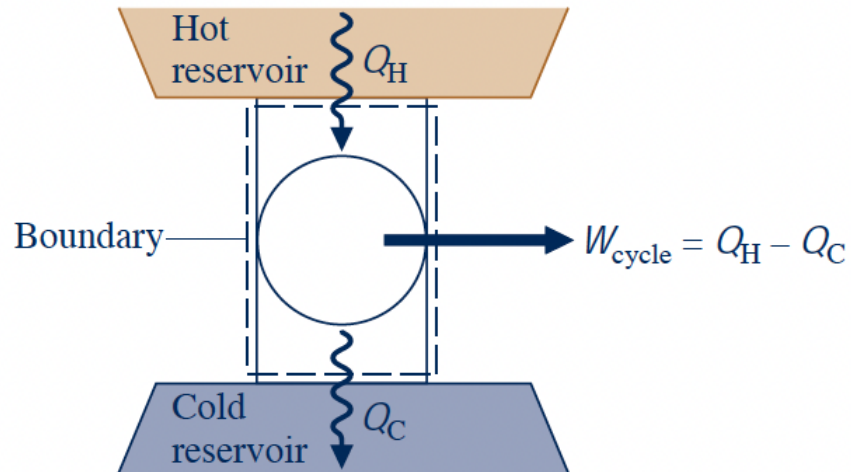
Clausius statement. It is impossible for any system to operate in such a way that the sole result would be an energy transfer by heat from a cooler to a hotter body.

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



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.

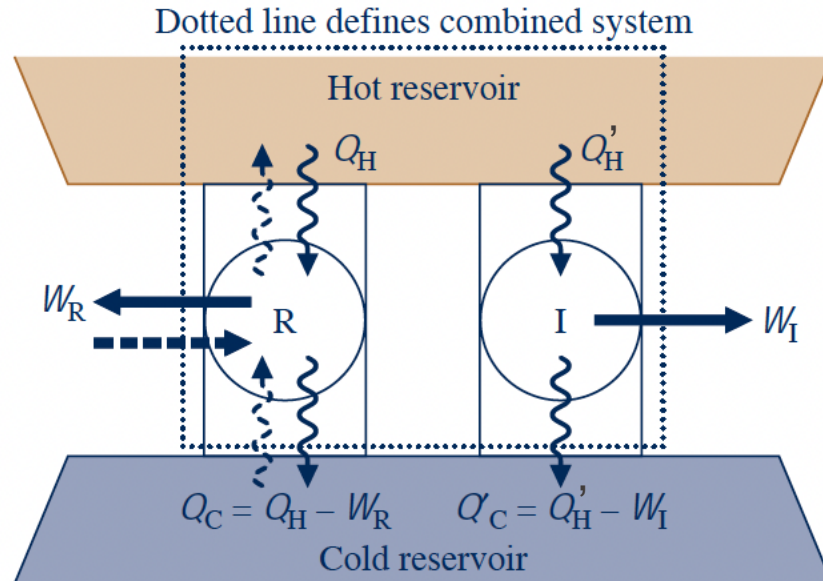
A **thermal reservoir** is a special kind of system that always remains at constant temperature even though energy is added or removed by heat transfer.



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

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.

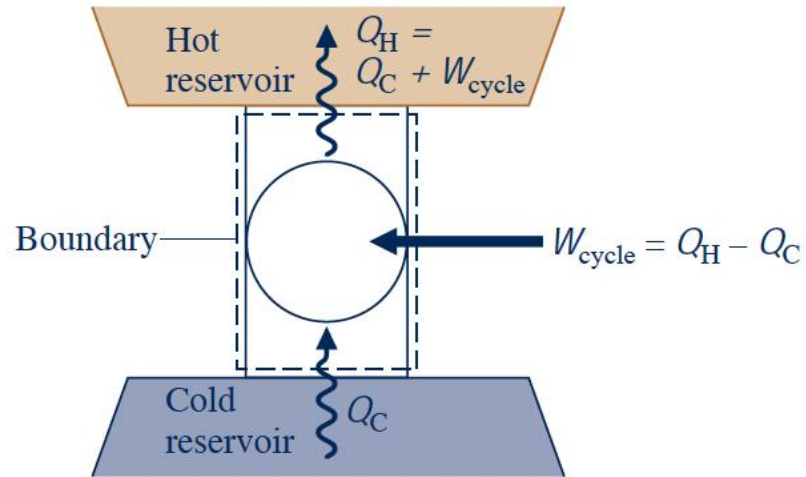


All reversible (Carnot) engines have the same universal efficiency $\eta(T_H, T_C)$

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



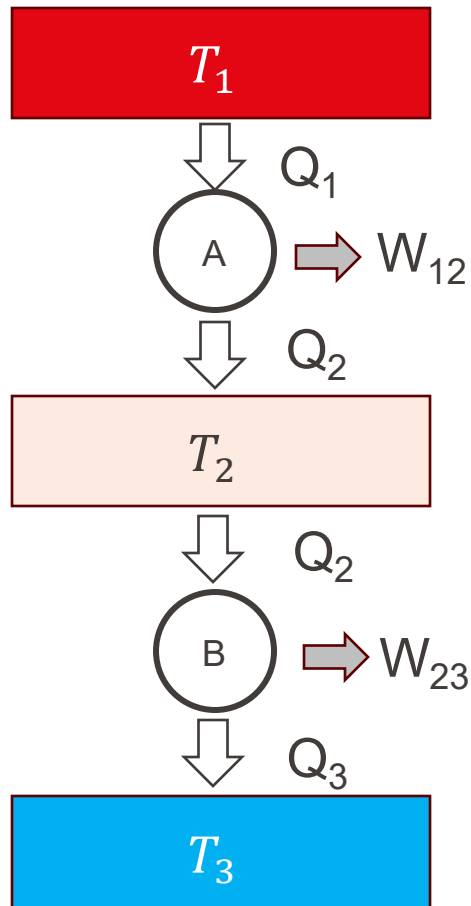
No refrigeration cycle operating between two thermal reservoirs has a higher COP than a reverse Carnot engine

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

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

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

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



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

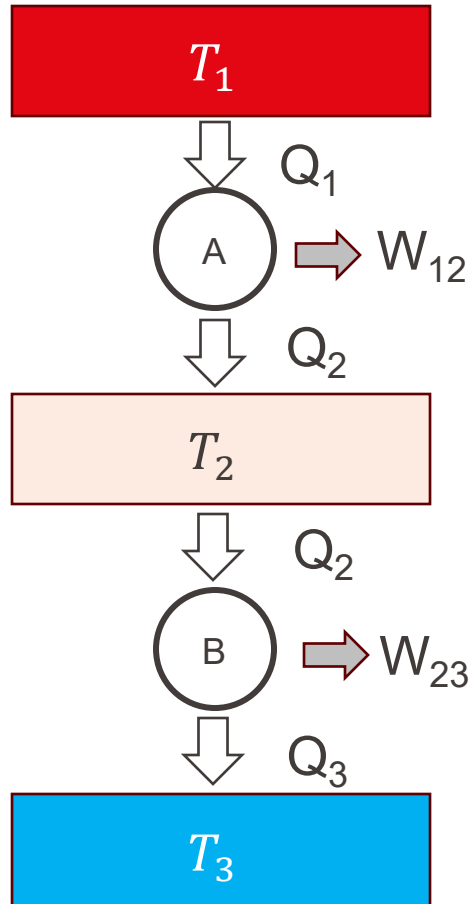
Heat dumped by the 1st engine is received by the 2nd

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

$$W_{13} = W_{12} + W_{23}$$

$$Q_1 \eta_c(T_1, T_3) = Q_1 \eta_c(T_1, T_2) + Q_2 \eta_c(T_2, T_3)$$

$$Q_1 \eta_c(T_1, T_3) = Q_1 \eta_c(T_1, T_2) + Q_1 (1 - \eta_c(T_1, T_2)) \eta_c(T_2, T_3)$$



$$1 - \eta_c(T_1, T_3) = (1 - \eta_c(T_1, T_2))(1 - \eta_c(T_2, T_3))$$

for any $T_1 > T_2 > T_3$

This implies $1 - \eta_c(T_1, T_2)$ takes the form of $f(T_2)/f(T_1)$, which by convention is set to be T_2/T_1

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1} \quad \text{defines the temperature up to a proportionality through the Carnot engine}$$

If we choose the triple point of water as 273.16 degree, we obtain the Kelvin scale [K]

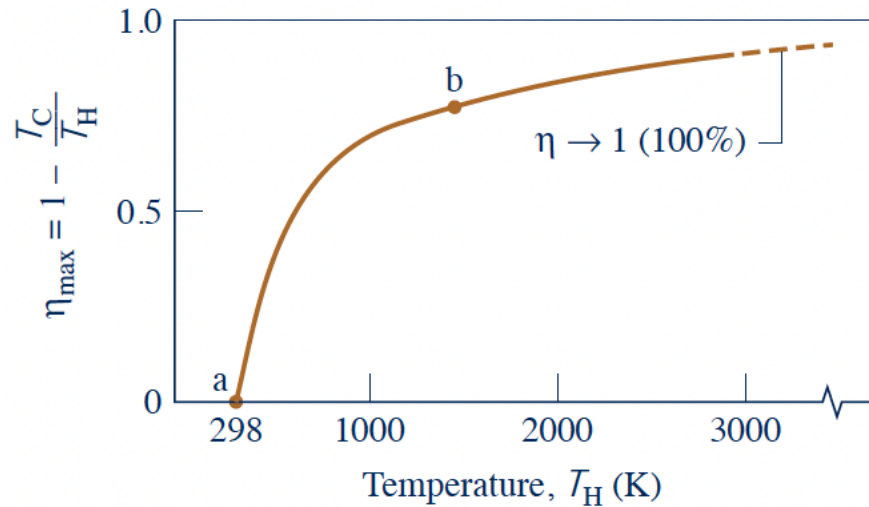
A theoretical approach to define temperature through Carnot engines, not practically useful, but independent of substances (conceptually clean)

All thermodynamic temperatures are positive

$\eta_c(T_1, T_2) = 1 - T_2/T_1$ cannot be greater than 1

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

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



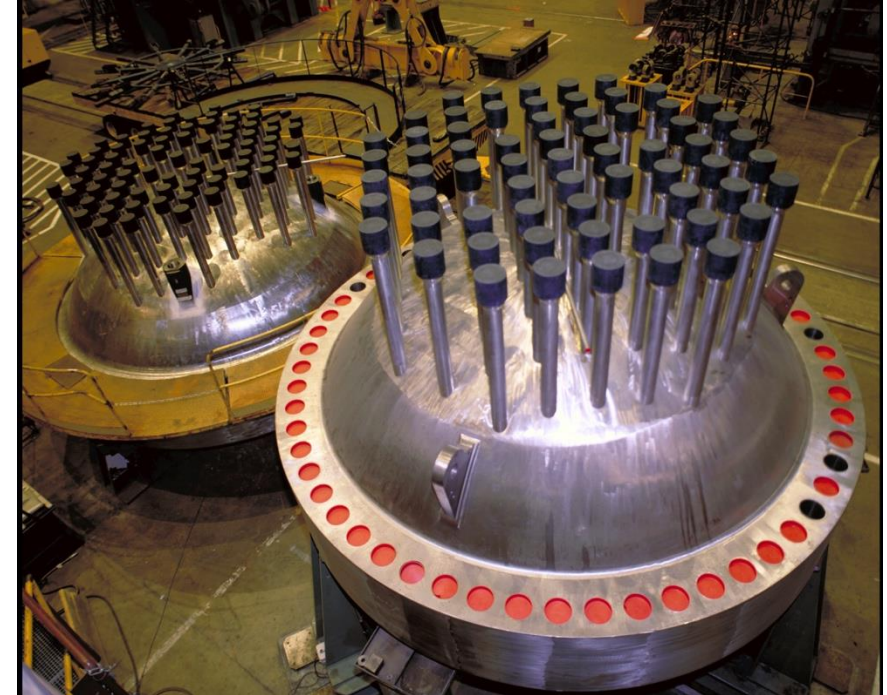
One effective approach to increase the maximum efficiency of power plants is to increase the hot-side temperature

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



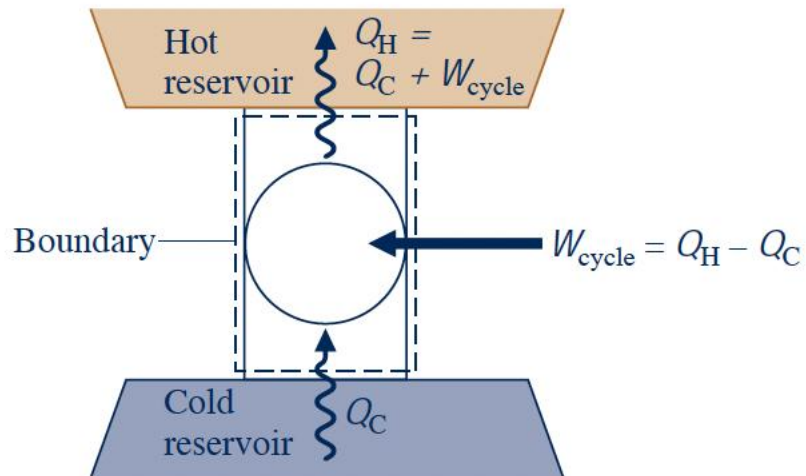
Credit: Koza1983, CC BY 3.0

Concentrated solar power plant



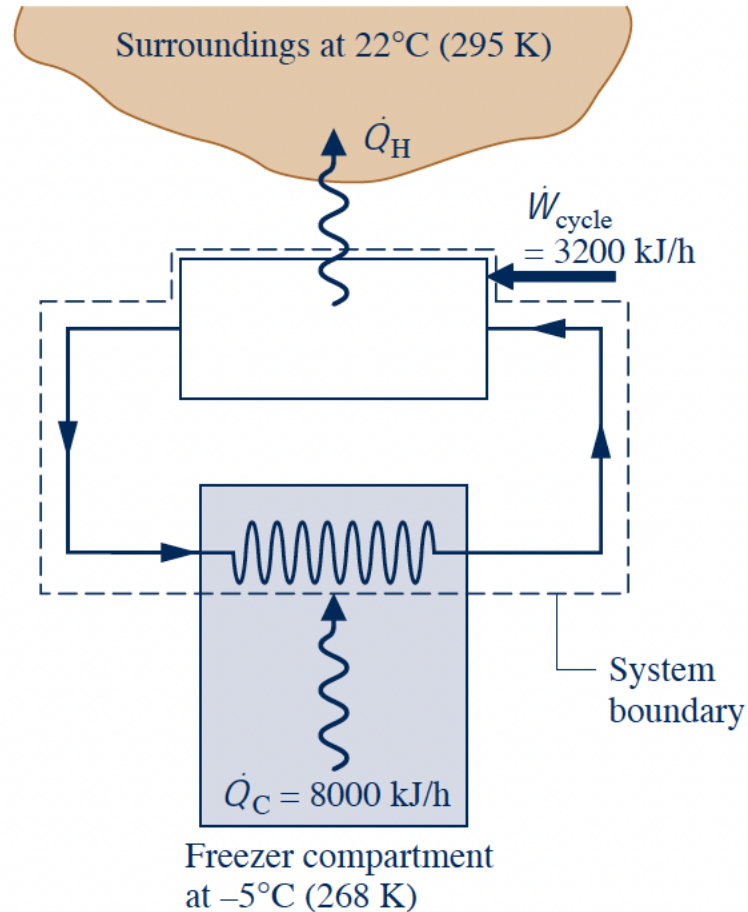
Credit: NRC

Pressurized water nuclear reactor



Refrigeration COP: $\beta_{\text{max}} = \beta_c = T_C / (T_H - T_C)$

Heat pump COP: $\gamma_{\text{max}} = \gamma_c = T_H / (T_H - T_C)$



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

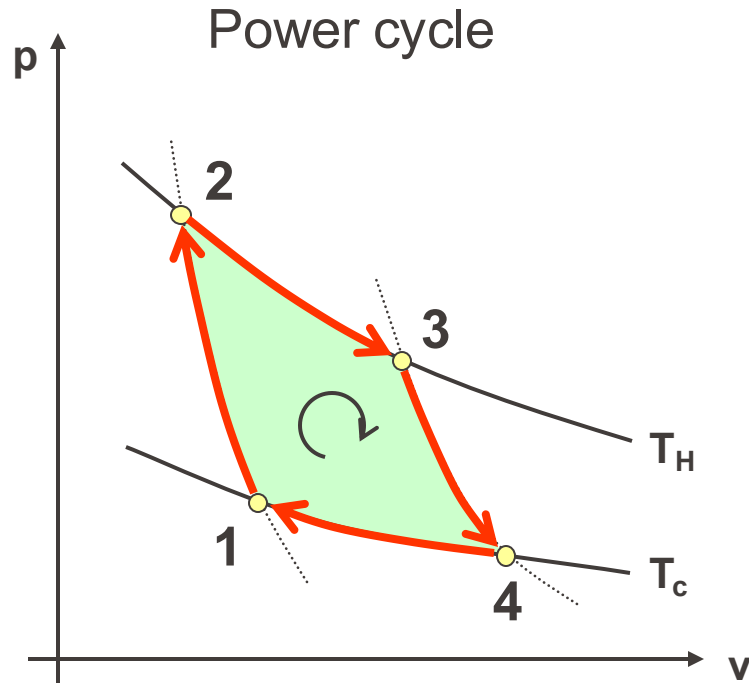
The heat transfer rate from the refrigerated space and the power input are known

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

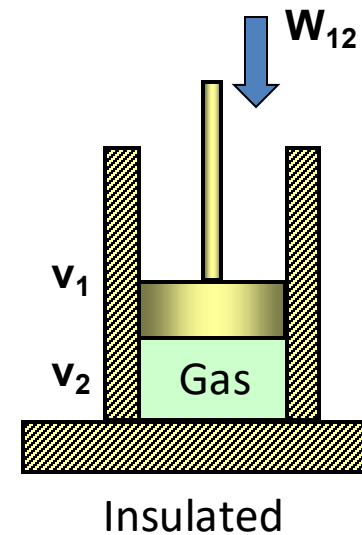
$$\text{Maximum COP } \beta_{max} = \frac{T_C}{T_H - T_C} = 9.9$$

$$\text{Actual COP } \beta = \frac{\dot{Q}_C}{\dot{W}_{cycle}} = 2.5$$

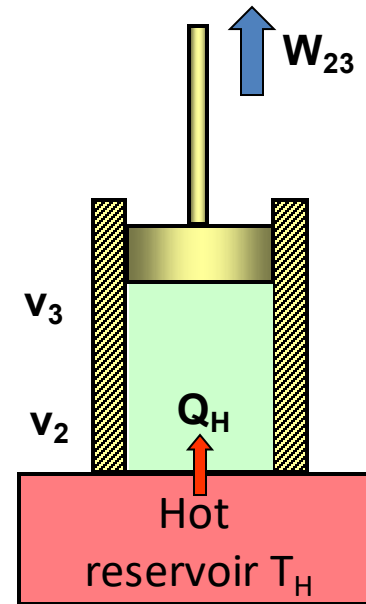
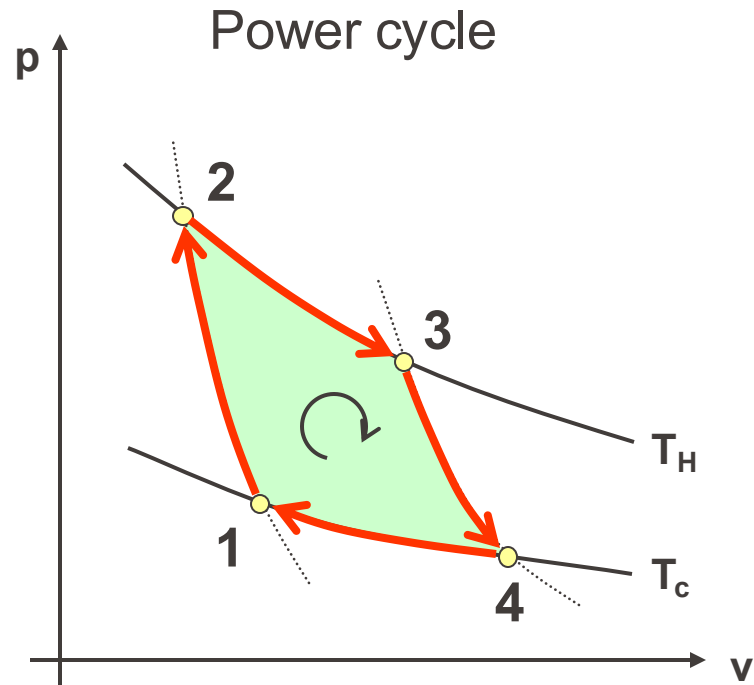
A reversible cycle that undergoes four reversible processes: two adiabatic processes alternated with two isothermal processes.

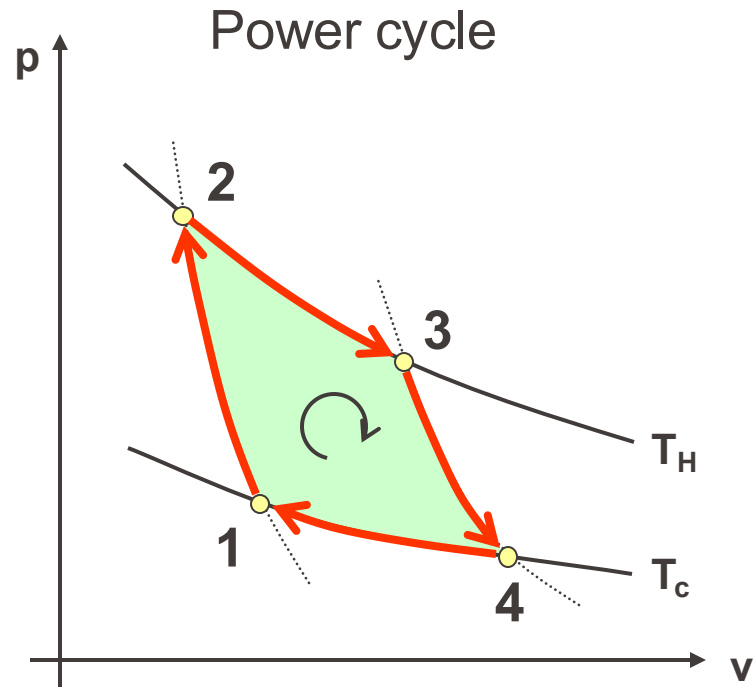


1-2 adiabatic compression

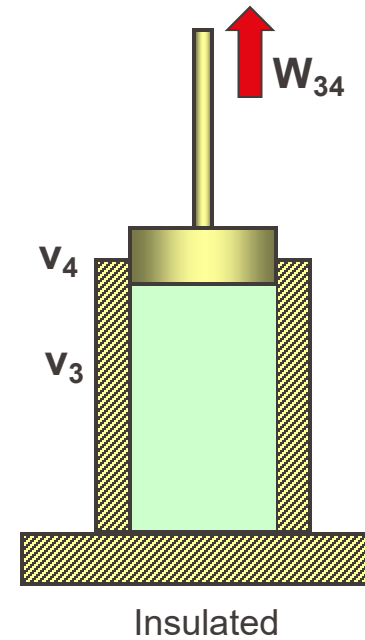


2-3 isothermal expansion receiving heat

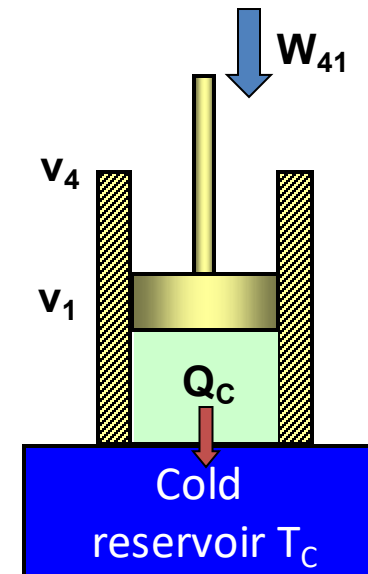
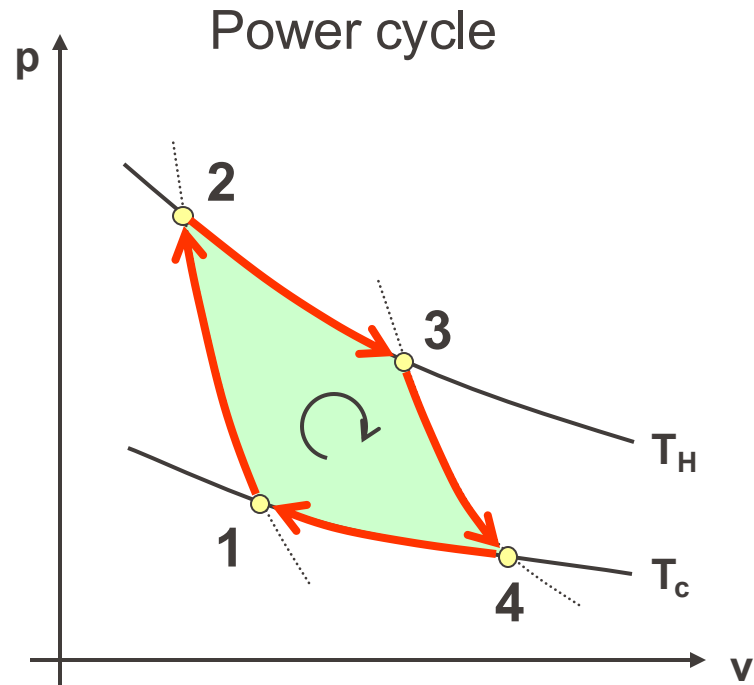


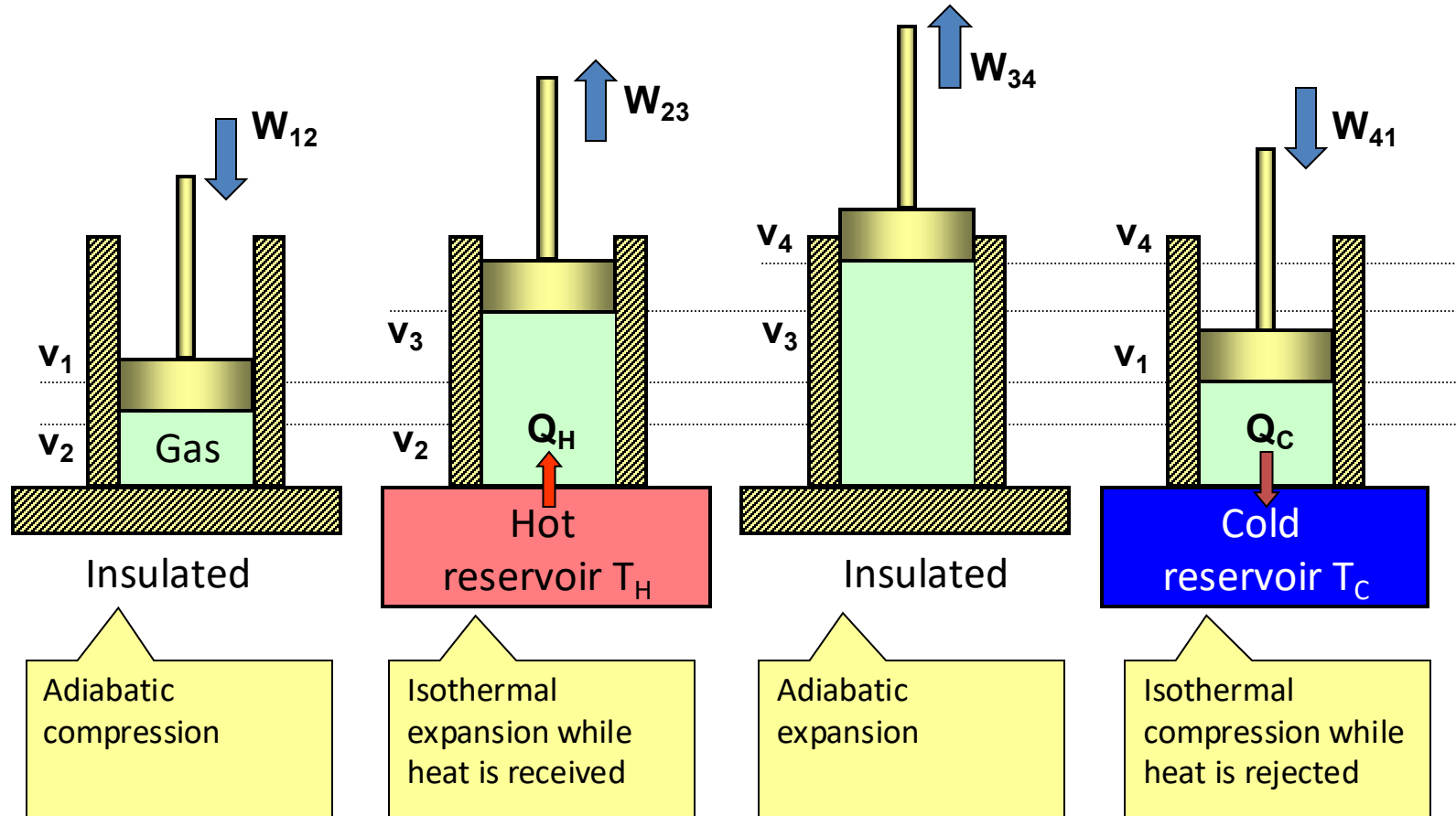


3-4 adiabatic expansion

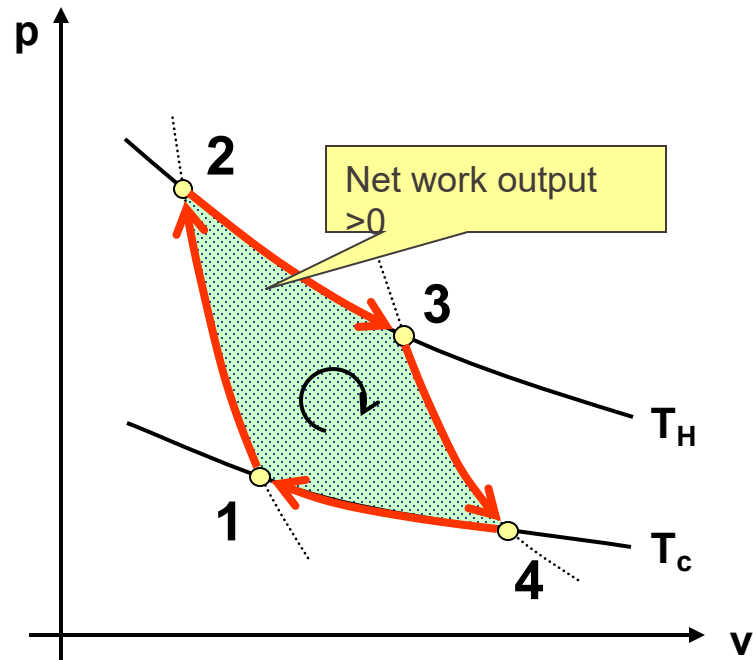


4-1 Isothermal compression discharging heat

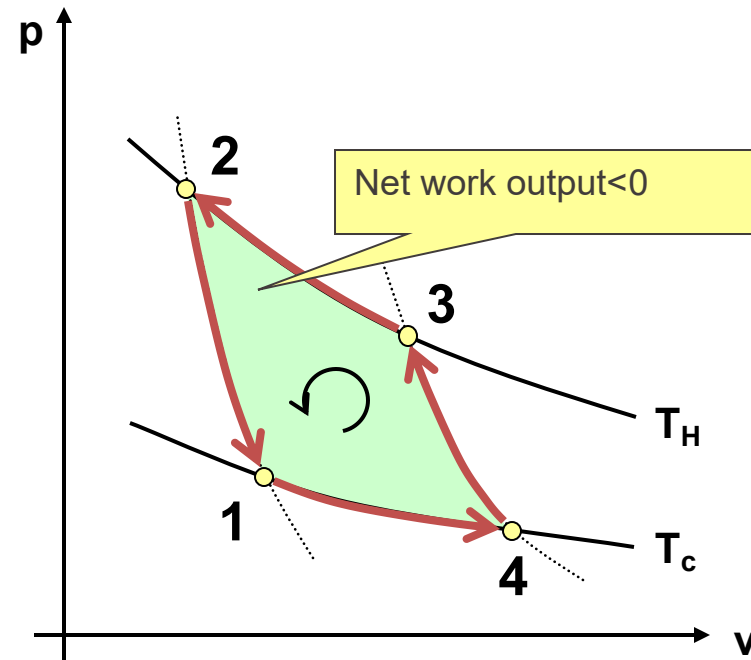




Power Cycle

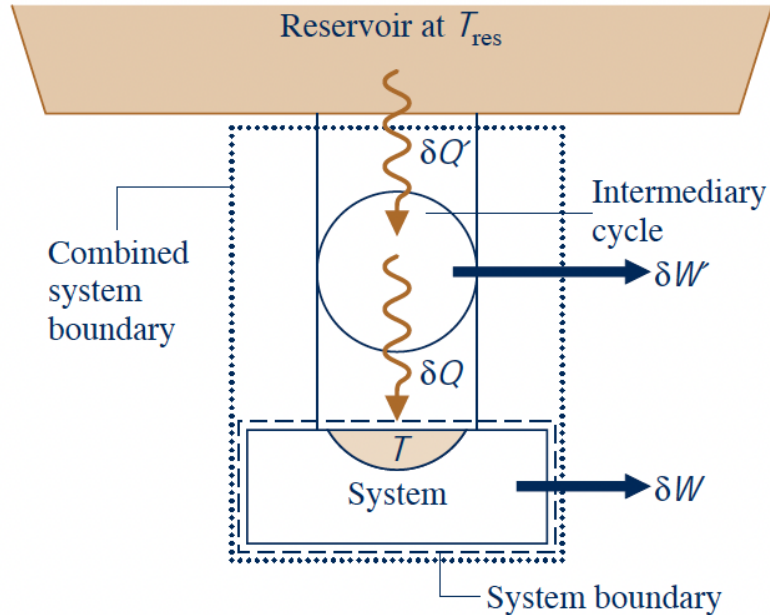


Refrigeration cycle



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
(negative value means heat flowing out of the system)



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)

Heat extracted from the top reservoir

$$\delta Q' = T_{res} \cdot \frac{\delta Q}{T}$$

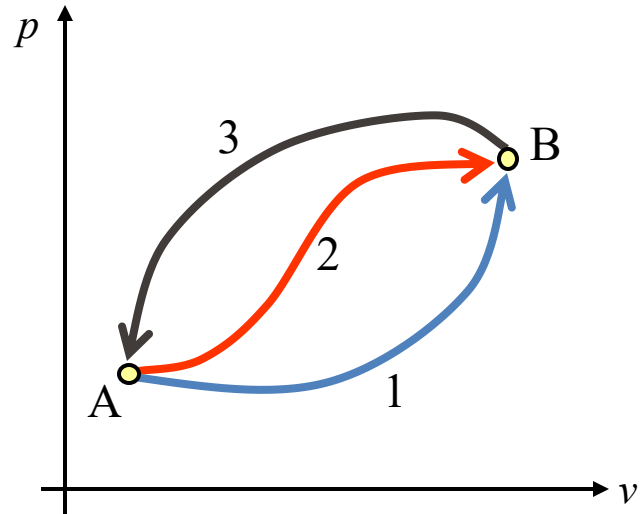
When the cycle is over, consider the combined system including the Carnot engine and the original system

Based on the 1st law, the net work output of this combined system is $\oint \delta Q'$

Based on the 2nd law (Kelvin-Planck), $\oint \delta Q' \leq 0 \Rightarrow \oint \frac{\delta Q}{T} \leq 0$

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

If you run it backwards $\oint \frac{-\delta Q_{rev}}{T} \leq 0$ Therefore $\oint \frac{\delta Q_{rev}}{T} = 0$



For all reversible paths between two thermodynamics states

$$\int_A^B \left(\frac{\delta Q_{rev}}{T} \right)_1 = \int_A^B \left(\frac{\delta Q_{rev}}{T} \right)_2 = - \int_B^A \left(\frac{\delta Q_{rev}}{T} \right)_3$$

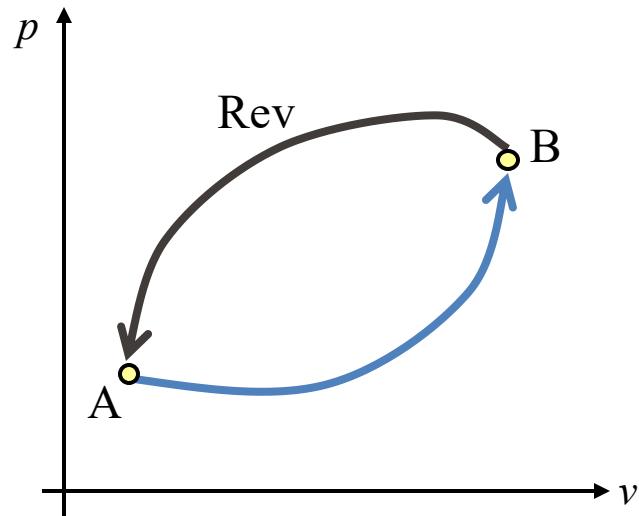
$$\int_A^B \frac{\delta Q_{rev}}{T} \text{ is path independent}$$

Construct a state function S

$$S(B) - S(A) = \int_A^B \frac{\delta Q_{rev}}{T} \quad dS = \frac{\delta Q_{rev}}{T}$$

This defines the entropy S up to a constant

$$S_A = S_{ref} + \int_{ref}^A \frac{\delta Q_{rev}}{T}$$



For any arbitrary change from A to B

$$\int_A^B \frac{\delta Q}{T} + \int_B^A \frac{\delta Q_{rev}}{T} \leq 0 \Rightarrow \int_A^B \frac{\delta Q}{T} \leq S(B) - S(A)$$

$$dS \geq \frac{\delta Q}{T}$$



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 $S = k_B \ln W$

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



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 \rightarrow higher uncertainty in location \rightarrow higher S

$$S_3 - S_2 = \frac{Q_{H,rev}}{T_H} > 0$$

Consider a differential reversible transformation from a certain state

$$dE = \delta Q_{rev} - \delta W_{rev}$$

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

$$dU = TdS - pdV$$

This relation is independent of the hypothetical reversible transformation

$$dH = dU + d(pV) = TdS + Vdp$$

In specific form: $du = Tds - pdv$ $dh = Tds + vdp$

For phase change $h_{fg} = T\Delta s_{fg}$

Incompressible substance

$$du = Tds - pdv \Rightarrow c(T)dT = Tds$$

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c(T)}{T} dT$$

For constant heat capacity, $s_2 - s_1 = c \ln \frac{T_2}{T_1}$

Ideal gas $du = Tds - pdv \Rightarrow c_v(T)dT = Tds - \frac{RT}{v} dv$

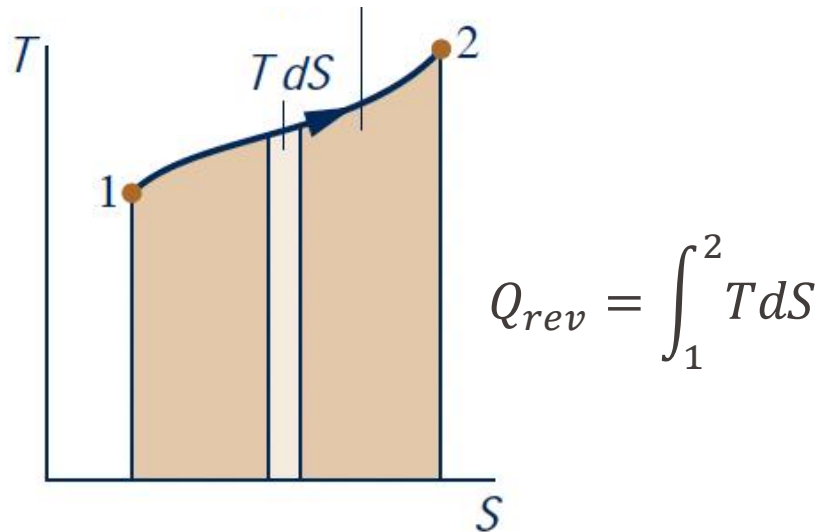
$$ds = c_v(T) \cdot \frac{dT}{T} + R \cdot \frac{dv}{v}$$

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_v(T)}{T} dT + R \ln \frac{v_2}{v_1} \quad \text{For perfect gas, } s_2 - s_1 = c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$$

Alternatively $dh = Tds + vdp \Rightarrow c_p(T)dT = Tds + \frac{RT}{p} dp$

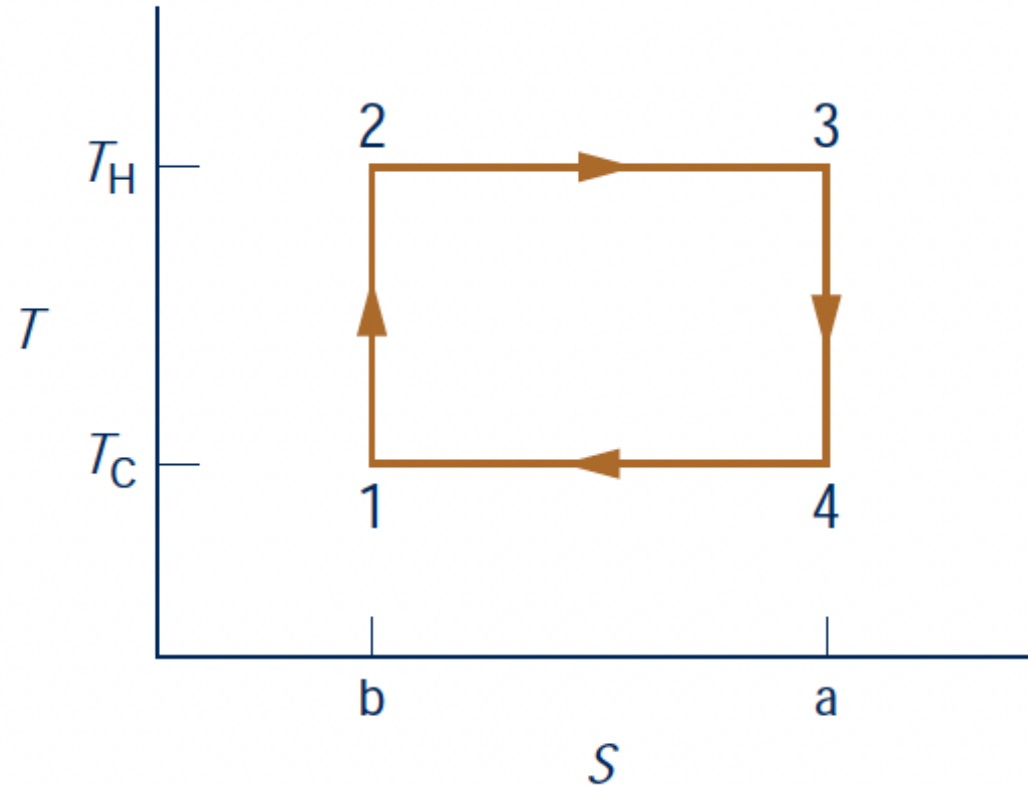
$$ds = c_p(T) \cdot \frac{dT}{T} - R \cdot \frac{dp}{p} \quad s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_p(T)}{T} dT - R \ln \frac{p_2}{p_1}$$

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



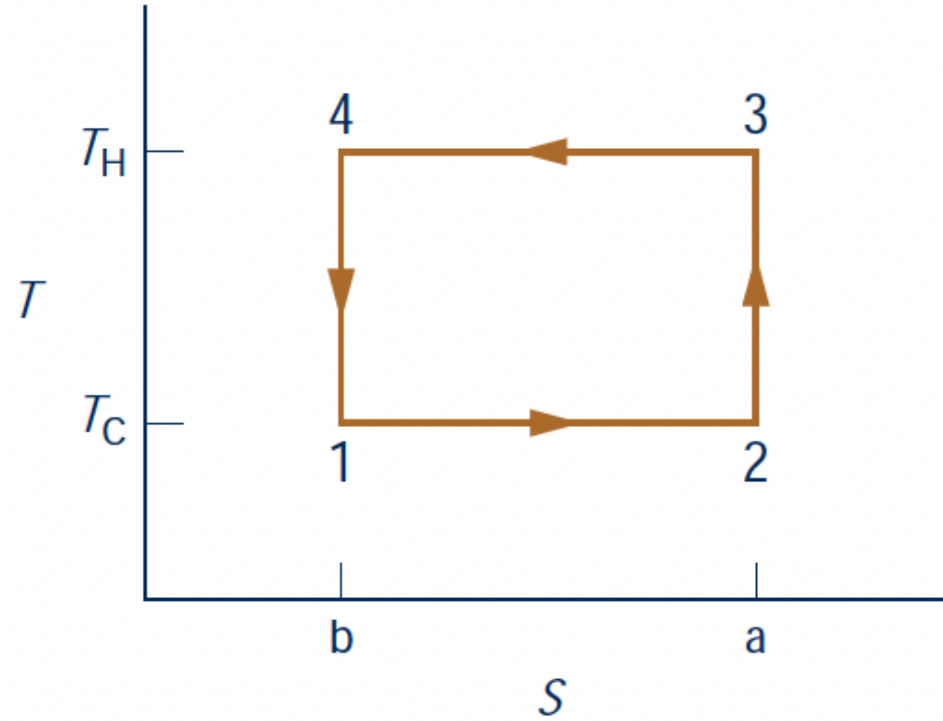
Temperature must be in Kelvin

Area only represents the reversible heat transfer



Power cycle efficiency

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



Refrigeration cycle COP

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