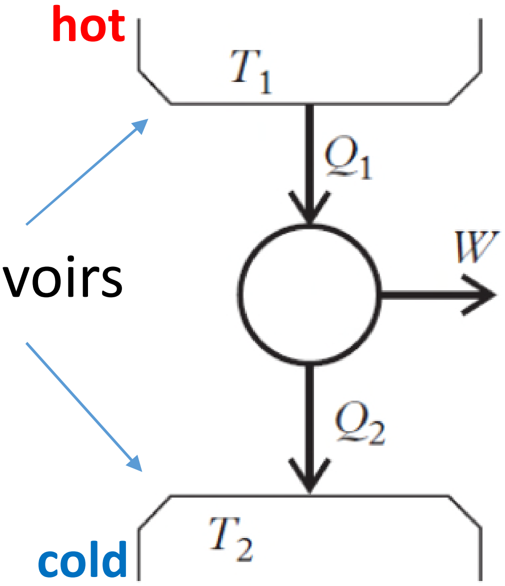
Thermodynamics lecture 4.

W.A.L.T.

- Carnot cycle
- Clausius and Kelvin statements imply one another
- Carnot’s theorem: efficiency of reversible heat engines
- The definition of absolute temperature
- Clausius’ theorem
- → ENTROPY!

“Heat engine”



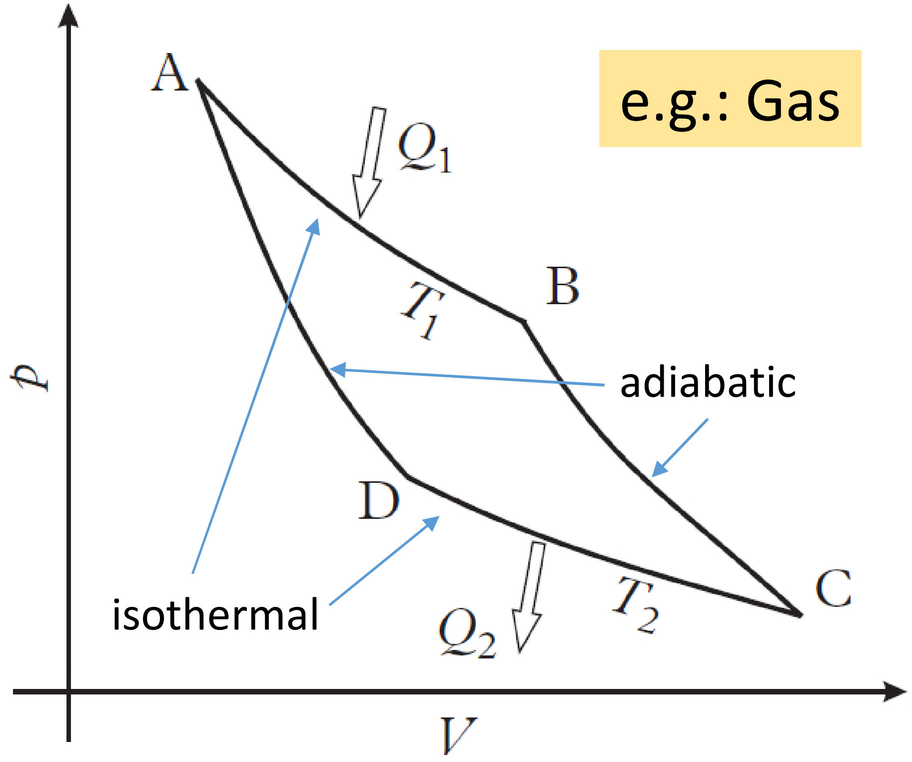
Thermal reservoirs

work output

Carnot cycle:

2 adiabatic and

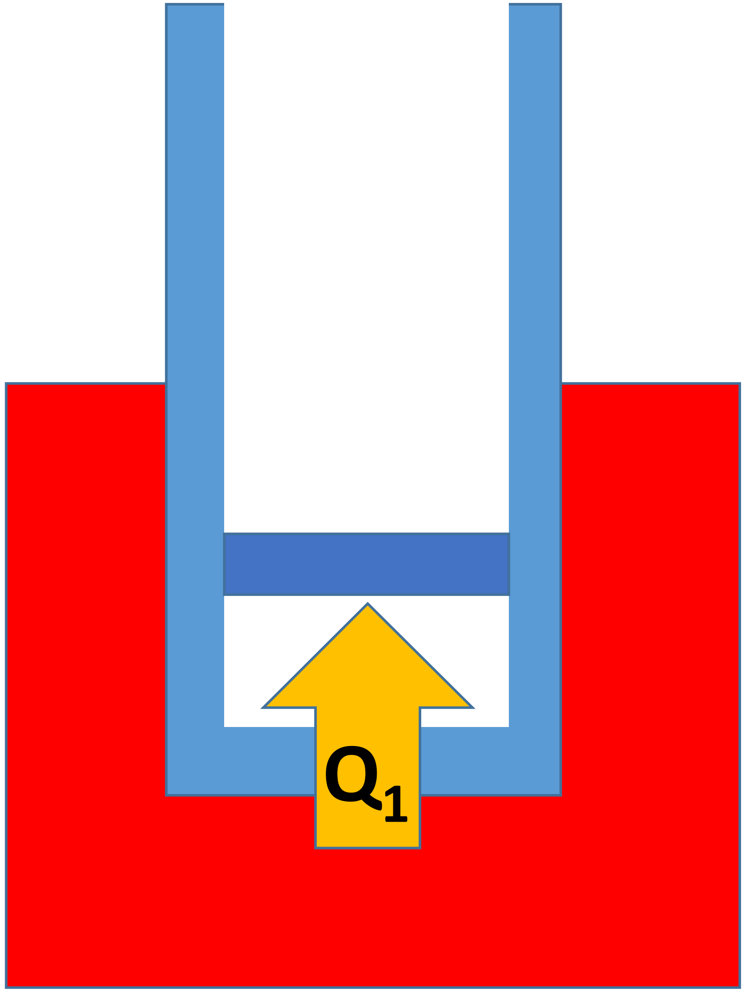
2 isothermal stages



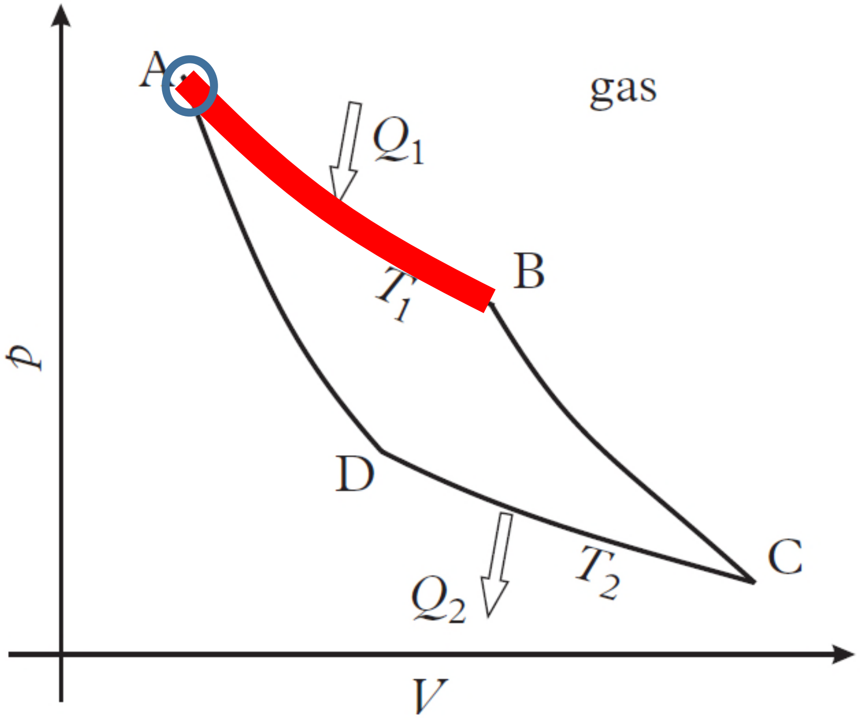
e.g.: Gas

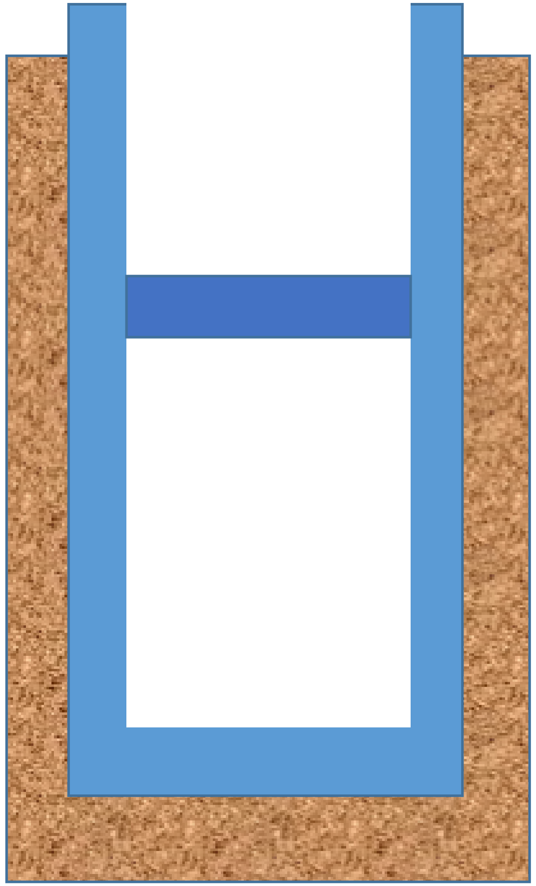
adiabatic

isothermal

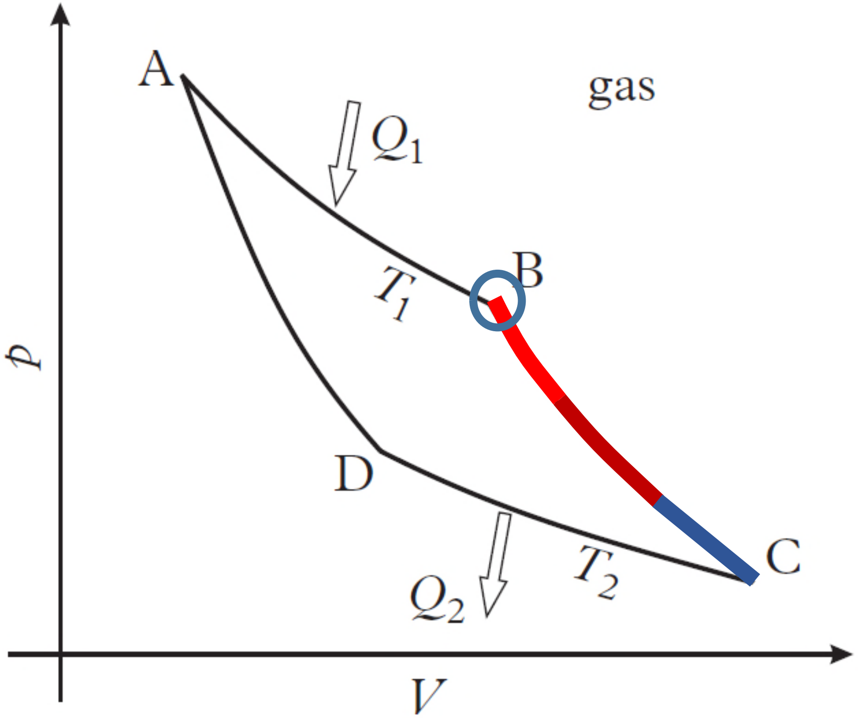


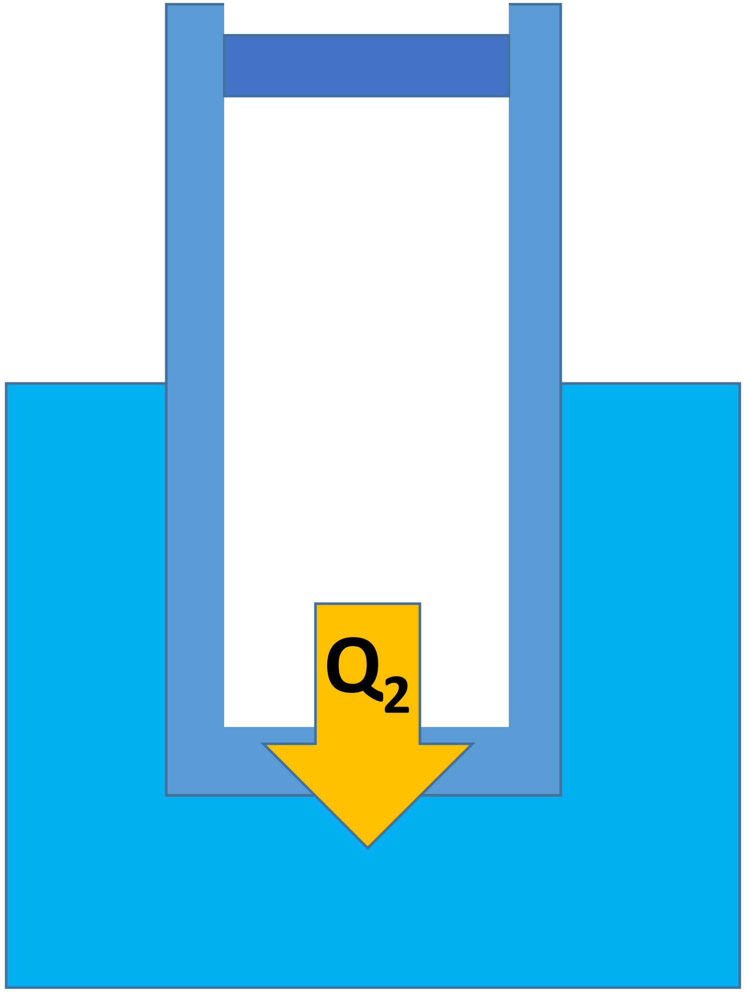
1. Thermal contact between the container and hot reservoir;
   allow the fluid to expand.



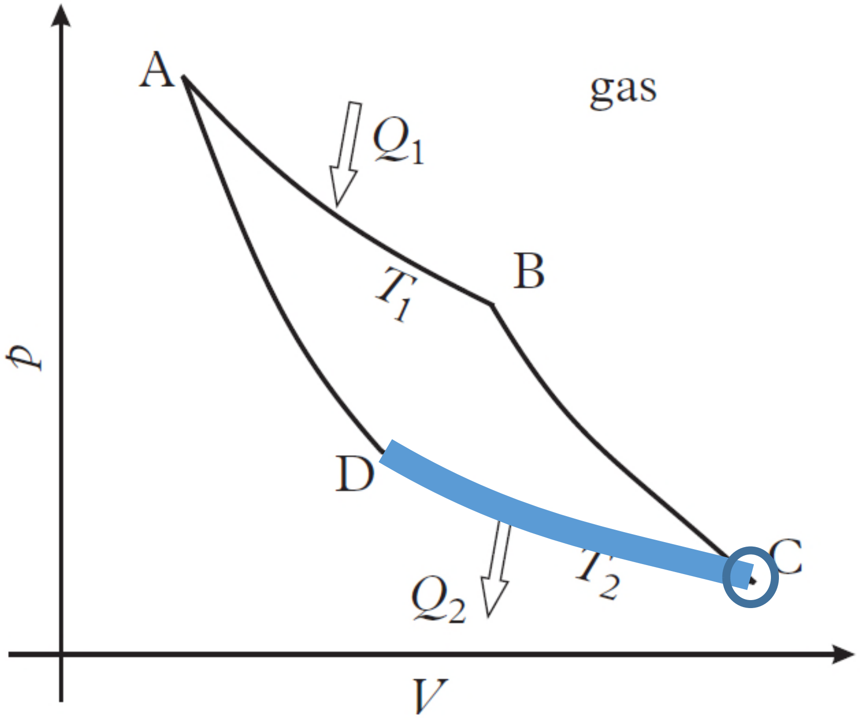


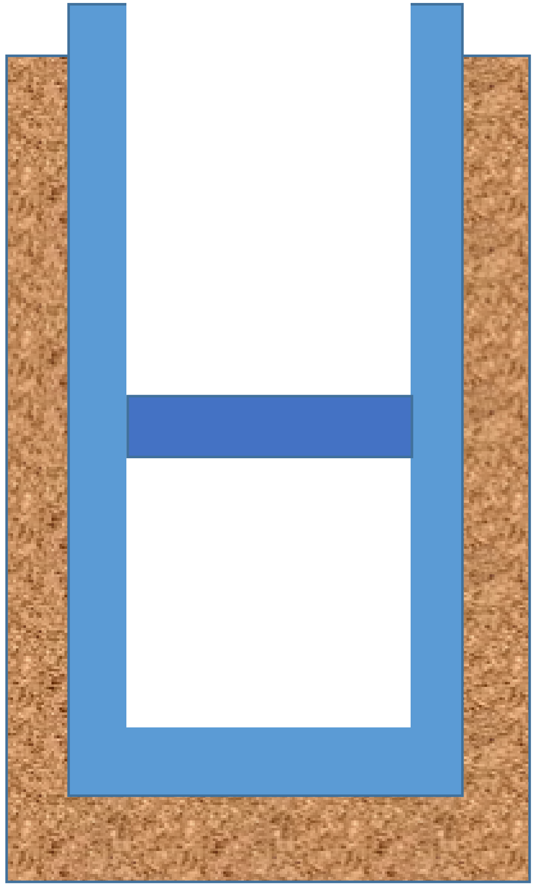
2. Thermally isolate the fluid and have it expand some more (so the fluid cools down).



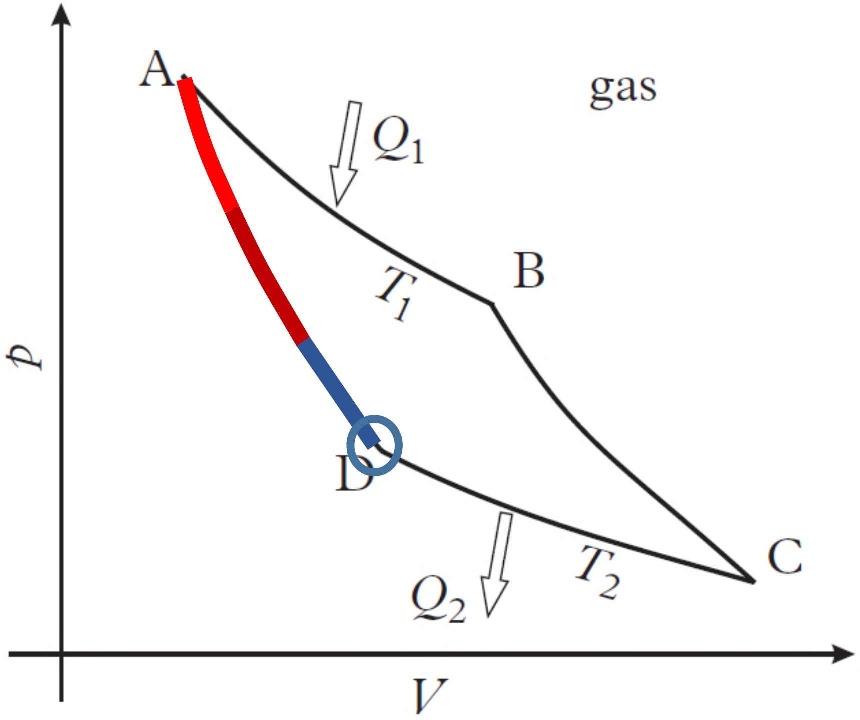


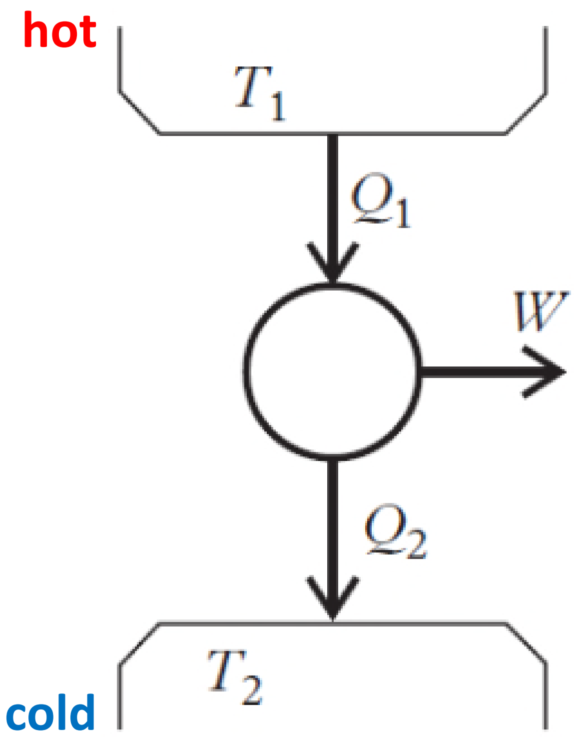
3. Contact the container with a cold reservoir and compress the fluid (the reservoir keeps it cool).



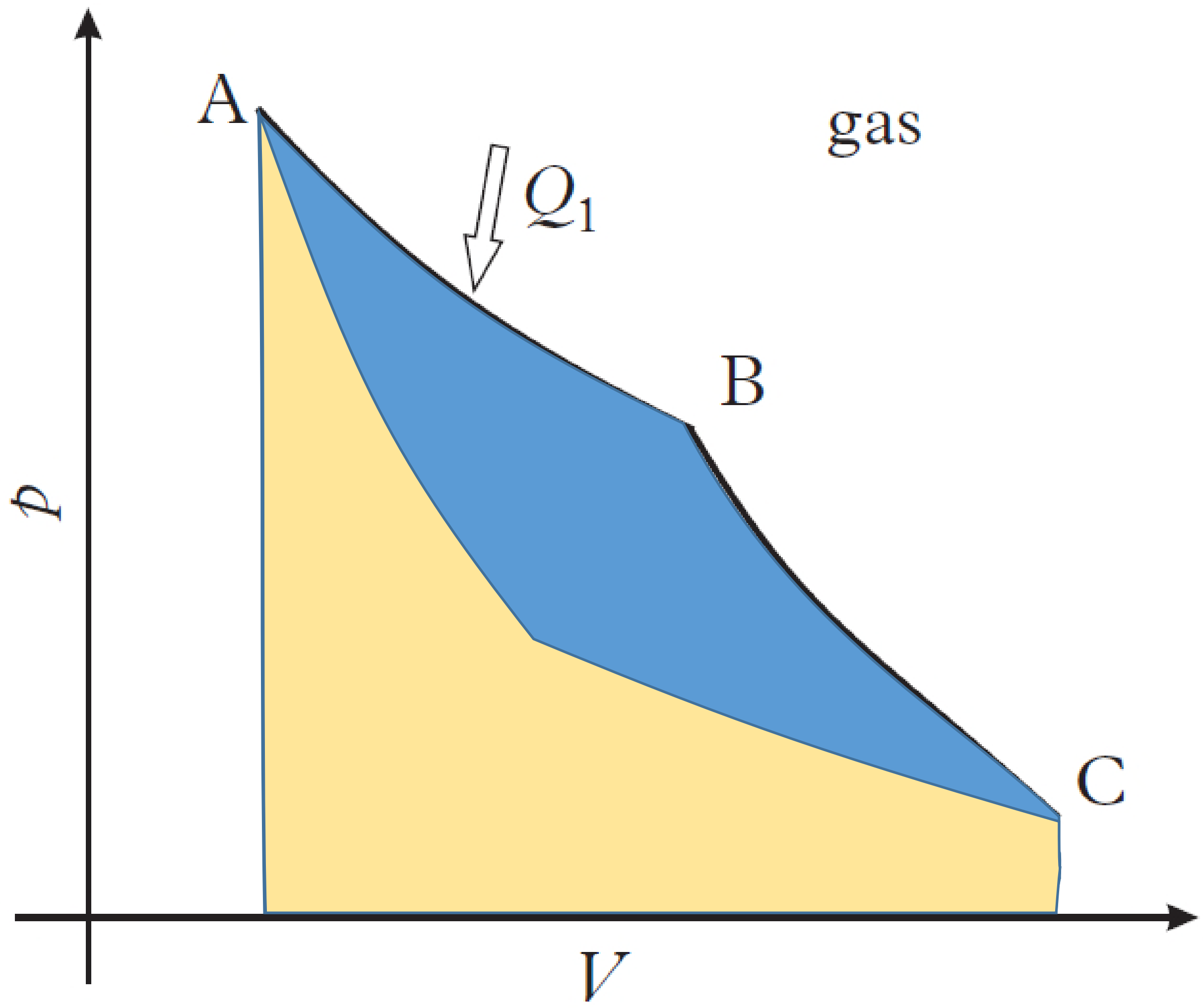


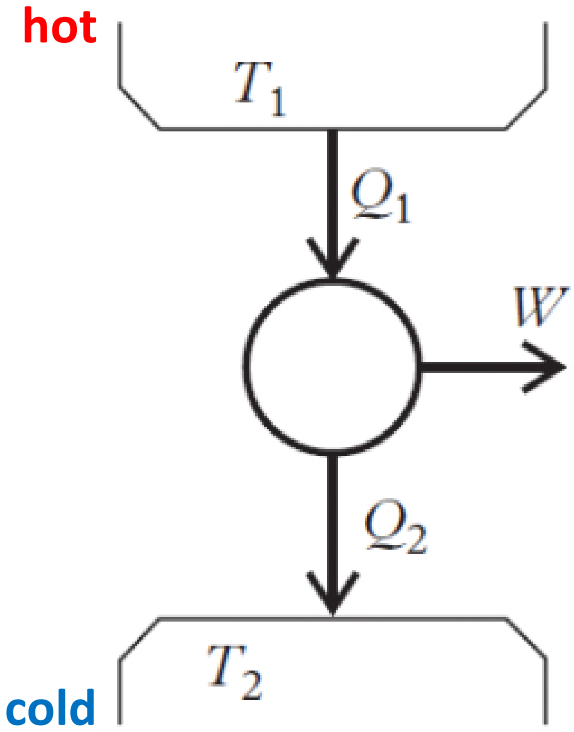
4. Thermally isolate the fluid and compress it some more (so it gets hotter).





$$W = Q_1 - Q_2$$





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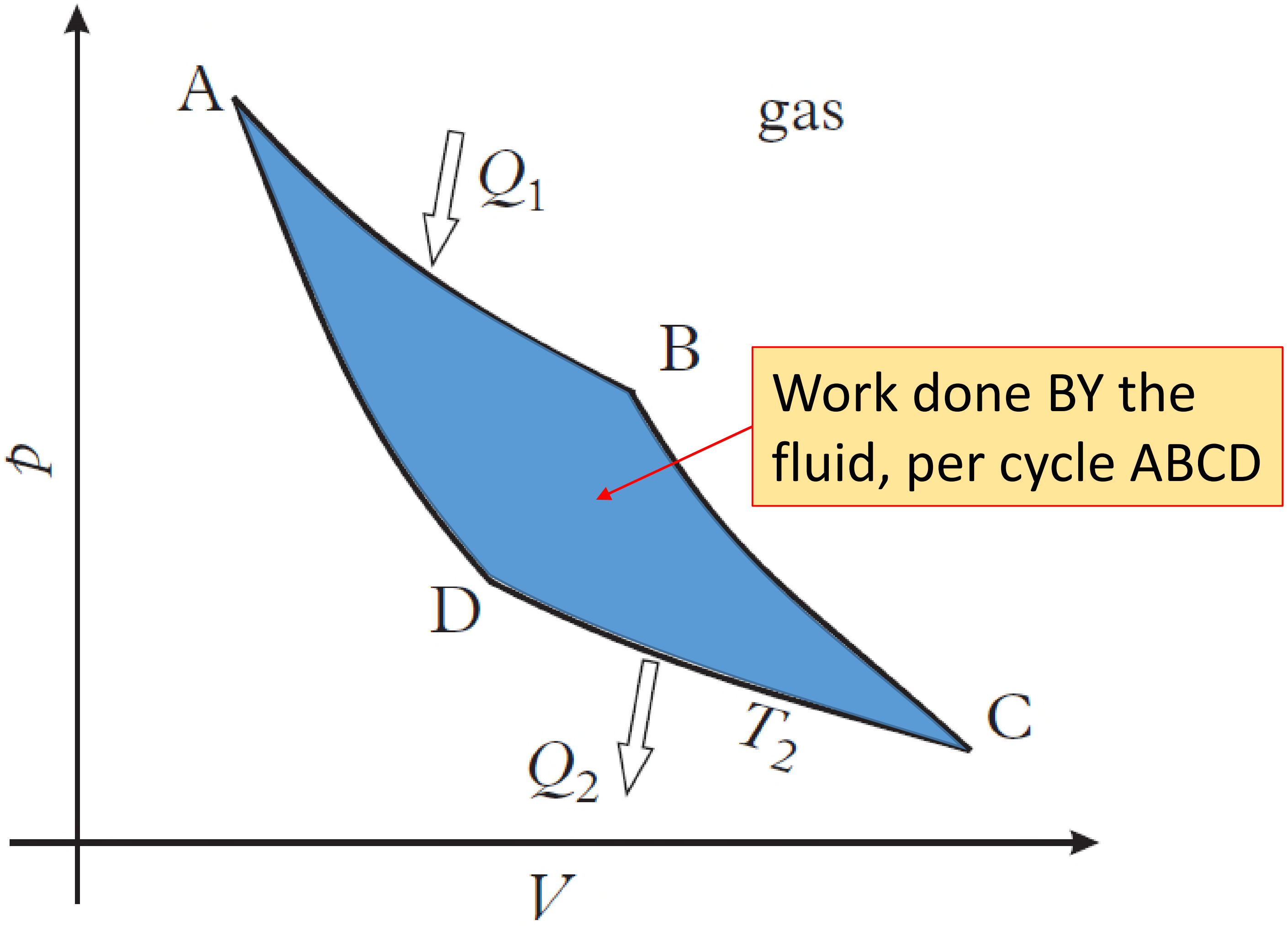
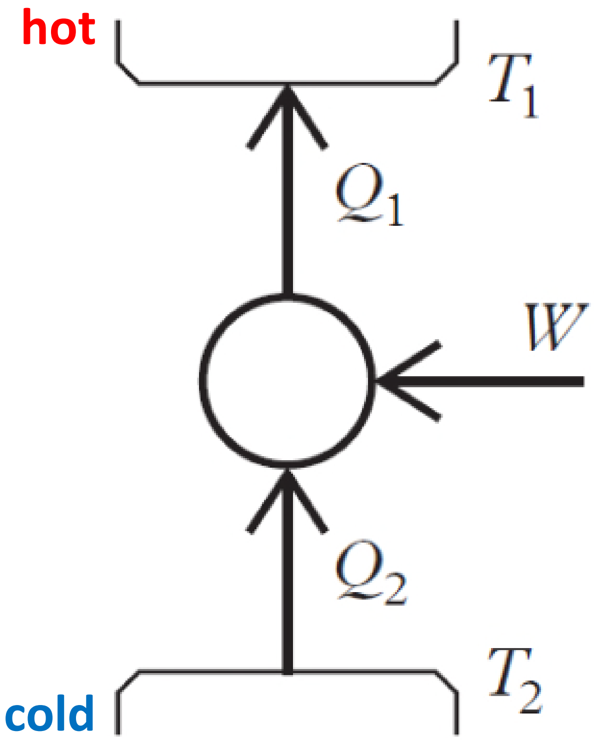


Work done BY the fluid, per cycle ABCD

We can run the same cycle in reverse:



Heat pump

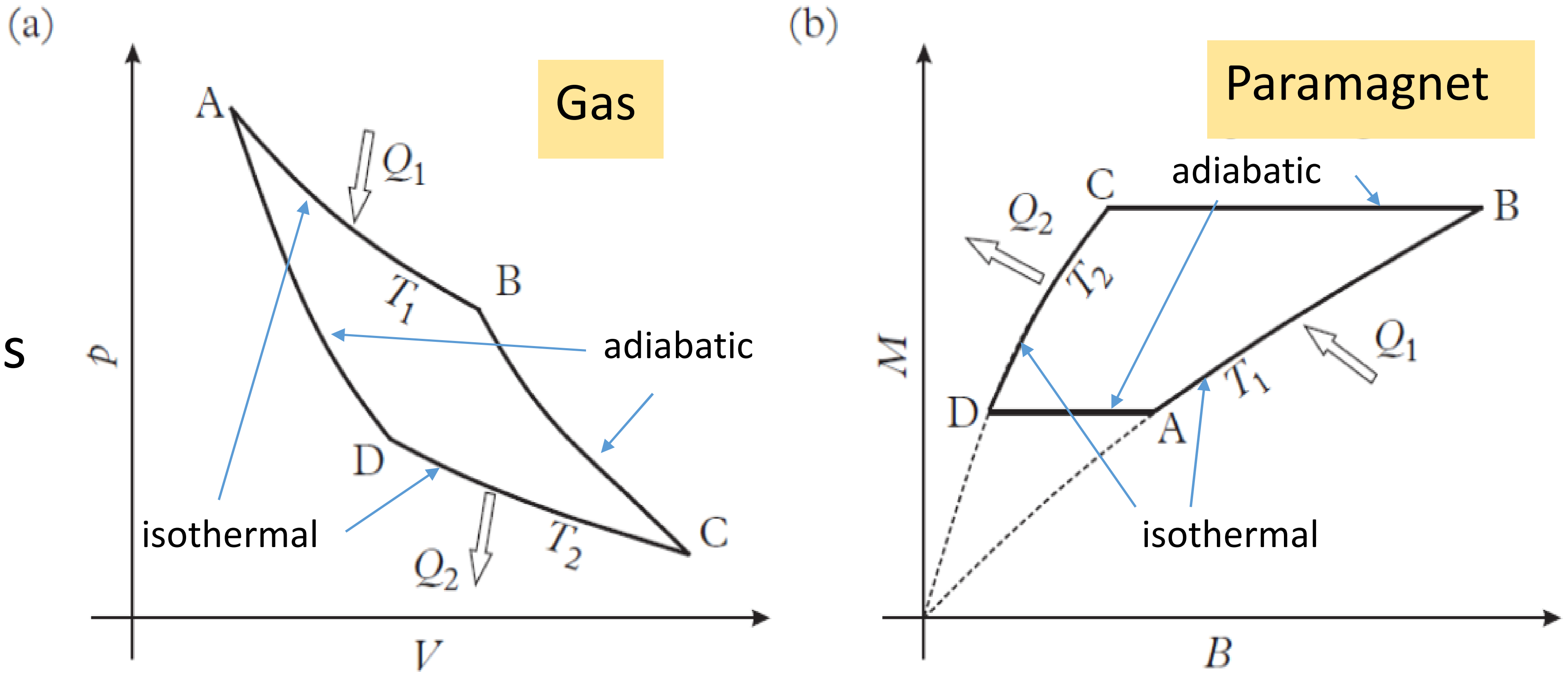
E.g.

- Refrigerator
- Air conditioning unit

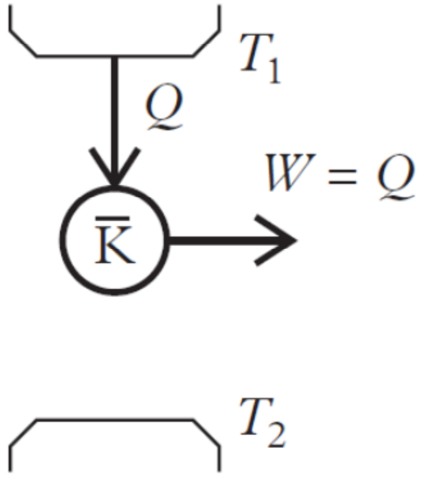
Any type of system can have a Carnot cycle:

Solid / liquid / gas
Magnetic
Electric
Soap film
Etc.

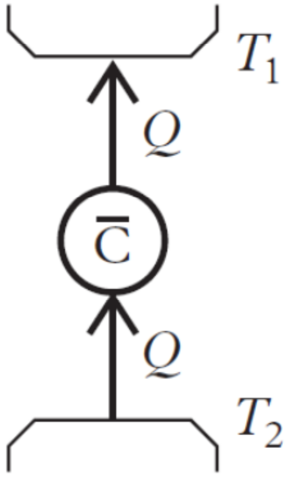
Carnot cycle:
2 adiabatic and
2 isothermal stages



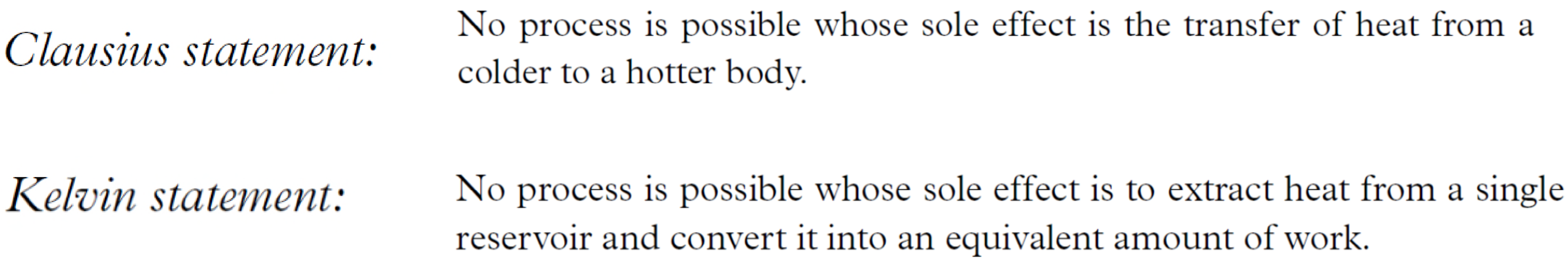
Proving that the Kelvin and Clausius statements of the Second Law imply one another.



Forbidden by
Kelvin statement



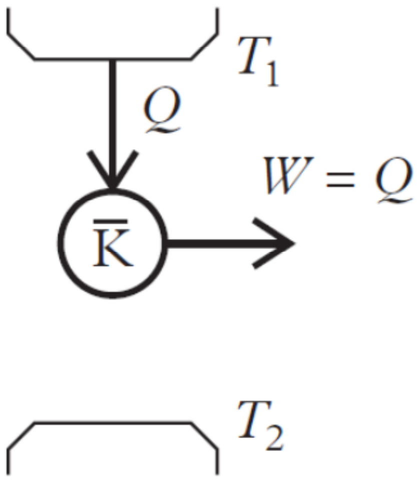
Forbidden by
Clausius statement



Clausius statement: No process is possible whose sole effect is the transfer of heat from a colder to a hotter body.

Kelvin statement: No process is possible whose sole effect is to extract heat from a single reservoir and convert it into an equivalent amount of work.

Proving that the Kelvin and Clausius statements of the Second Law imply one another.



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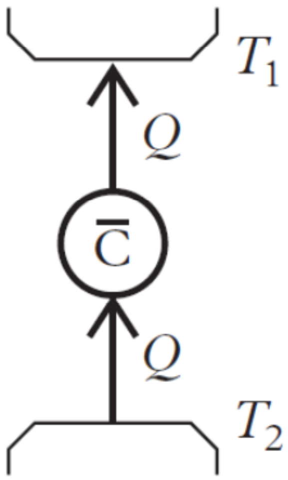

Forbidden by
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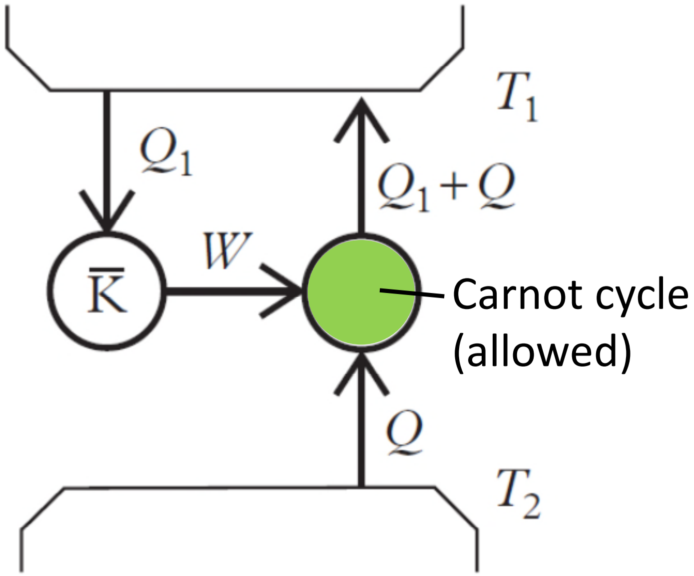
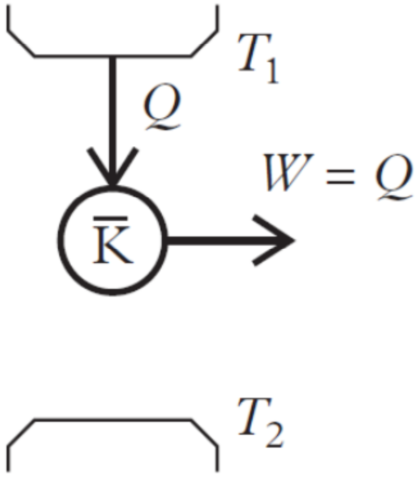


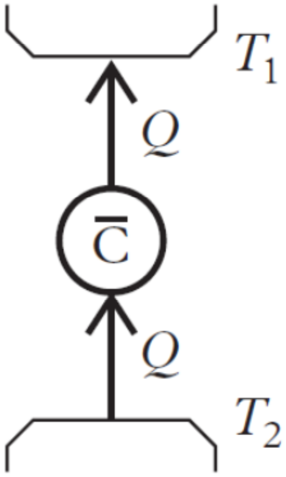
Carnot cycle
(allowed)

- Clausius statement of the 2nd Law says the net result here is physically impossible
- But we know the Carnot cycle is possible
- So the engine $\overline{\mathrm{K}}$ must be impossible
- … Which is the Kelvin statement of the 2nd Law

Proving that the Kelvin and Clausius statements of the Second Law imply one another.

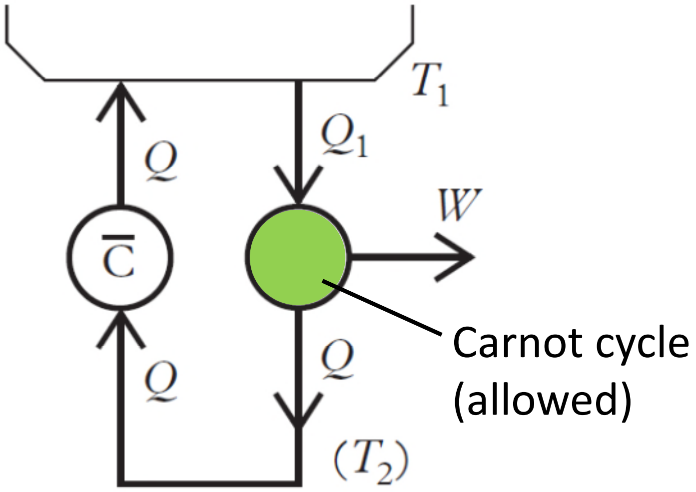


Forbidden by Kelvin statement

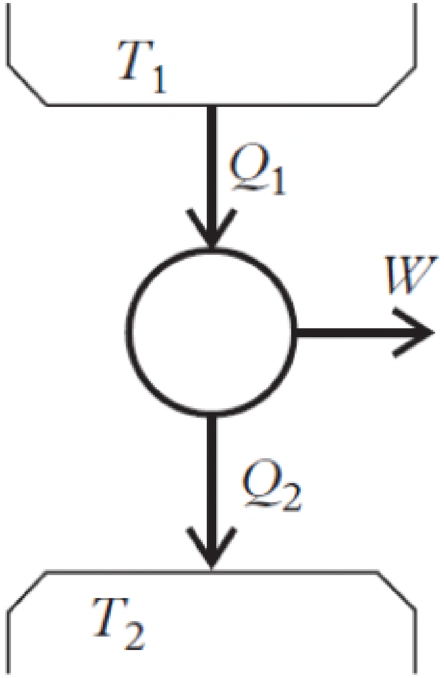


Forbidden by Clausius statement

- Kelvin statement of the 2nd Law says the net result here is physically impossible
- But we know the Carnot cycle is possible
- So the engine $\overline{\mathrm{C}}$ must be impossible
- … Which is the Clausius statement of the 2nd Law



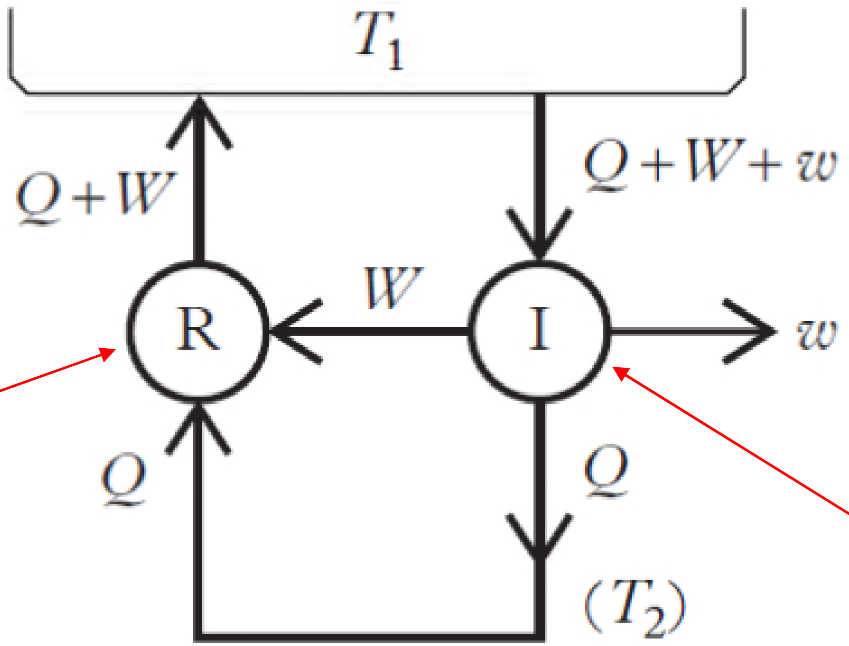
Definition of efficiency of a heat engine



$$W = Q_1 - Q_2$$

Efficiency $$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

Carnot’s theorem



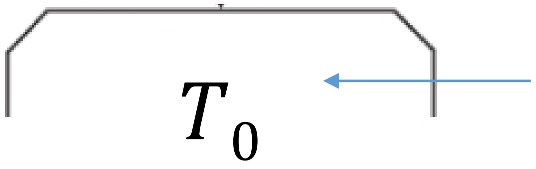
A physically possible reversible engine

A hypothetical engine which is more efficient than R

All reversible heat engines operating between given temperatures are equally efficient, and more efficient that non-reversible ones, no matter what the engines’ internal construction or physical parameters may be (whether pressure, or magnetic fields, or whatever).

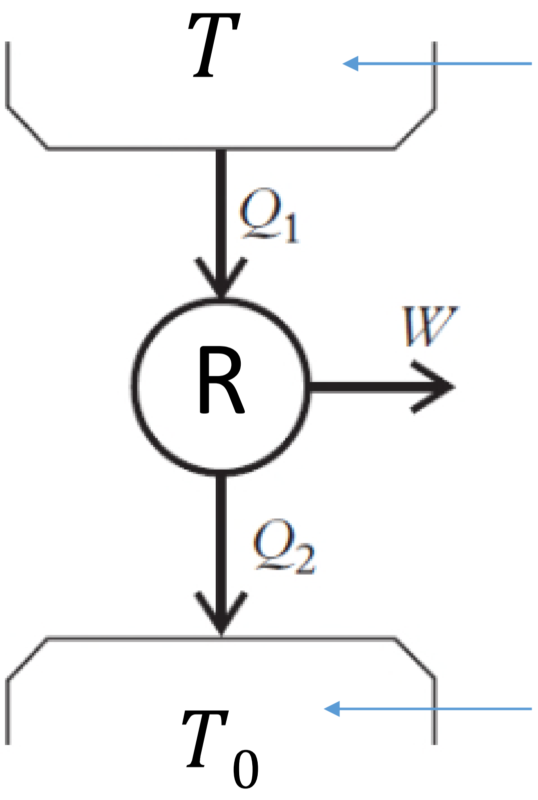
Definition of absolute temperature

Body in some arbitrary equilibrium state



A standard system in some chosen reference state
(we pick pure water, ice, steam in mutual equilibrium;
this is called the triple point of water).
Assign it some chosen temperature T_0 (e.g. 273.16 units)

Definition of absolute temperature

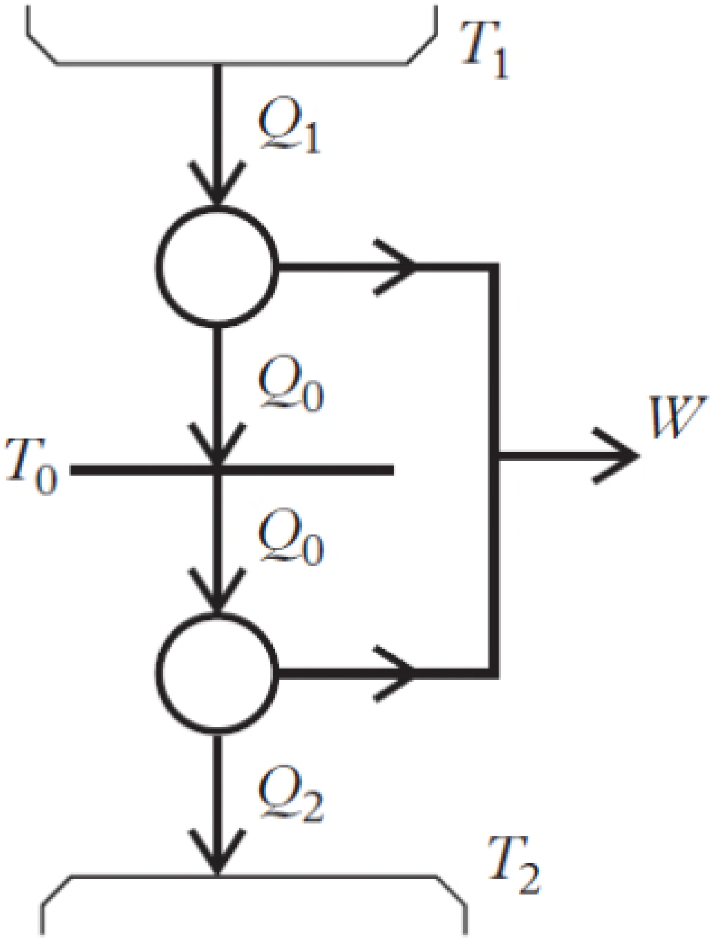


Body in some arbitrary equilibrium state

Define $T := \frac{Q_1}{Q_2} T_0$

A standard system in some chosen reference state
(we pick pure water, ice, steam in mutual equilibrium;
this is called the triple point of water).
Assign it some chosen temperature T_0 (e.g. 273.16 units)

Ratio of heats for a reversible engine

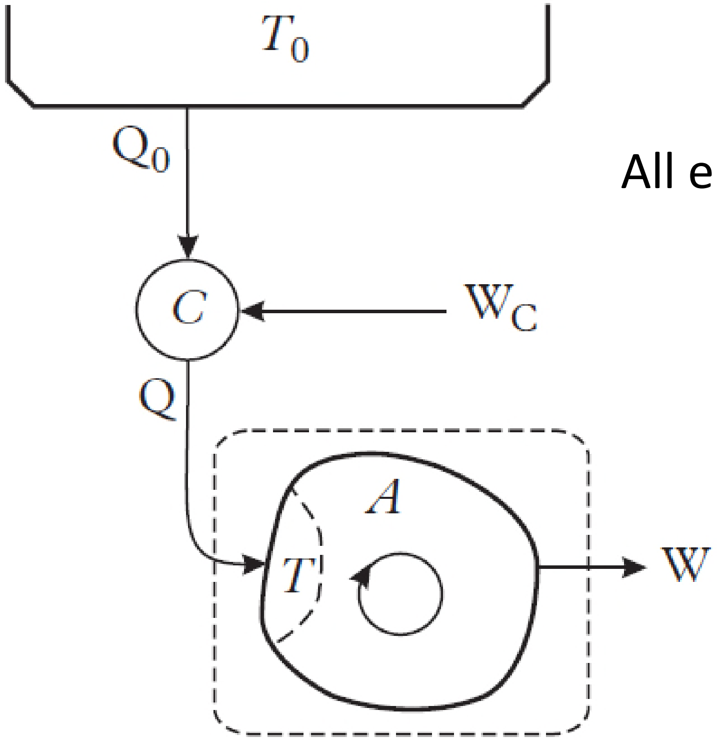


$$\boxed{\frac{Q_1}{Q_2} = \frac{T_1}{T_2}}$$

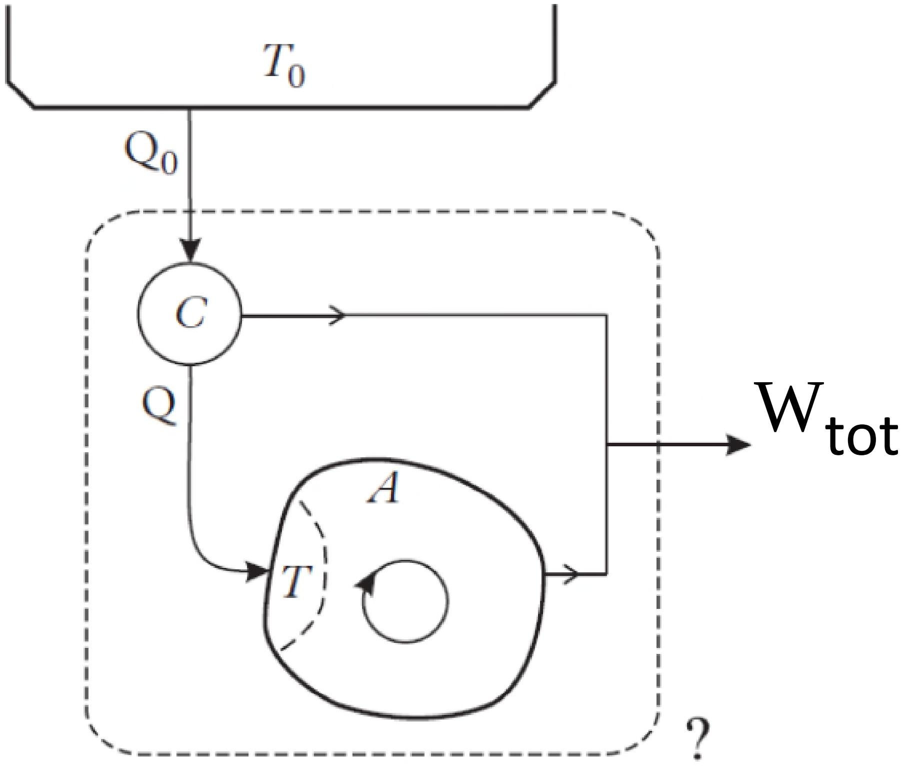
Hot heat is more valuable than cold heat

Heat energy delivered by a system at high temperature is more valuable (can be used to drive a greater variety of processes) than the same amount of heat at low temperature.

Next: **Clausius’ theorem**



All entirely possible!



Per cycle:

Net heat supplied to system: $Q = \oint \text{đ}Q$ Can be +ve or -ve

Net heat extracted from reservoir: $Q_0 = \oint \text{đ}Q_0 = T_0 \oint \frac{1}{T} \text{đ}Q \boxed{\leq 0}$

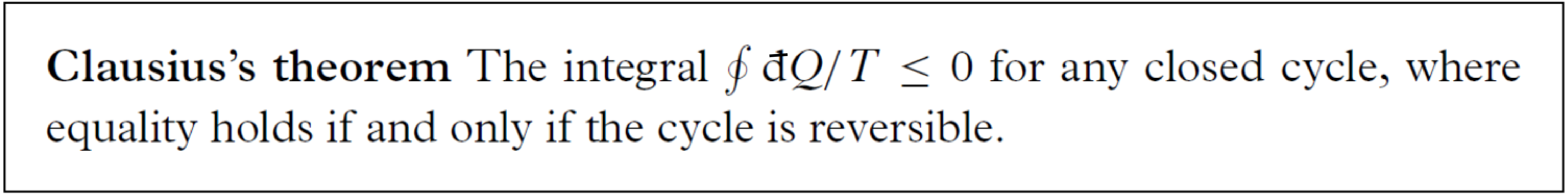
(Kelvin statement)

Clausius’ theorem, first part

For any cycle:

$$\oint \frac{1}{T}\,\text{đ}Q \leq 0.$$

Clausius’ theorem, in full:



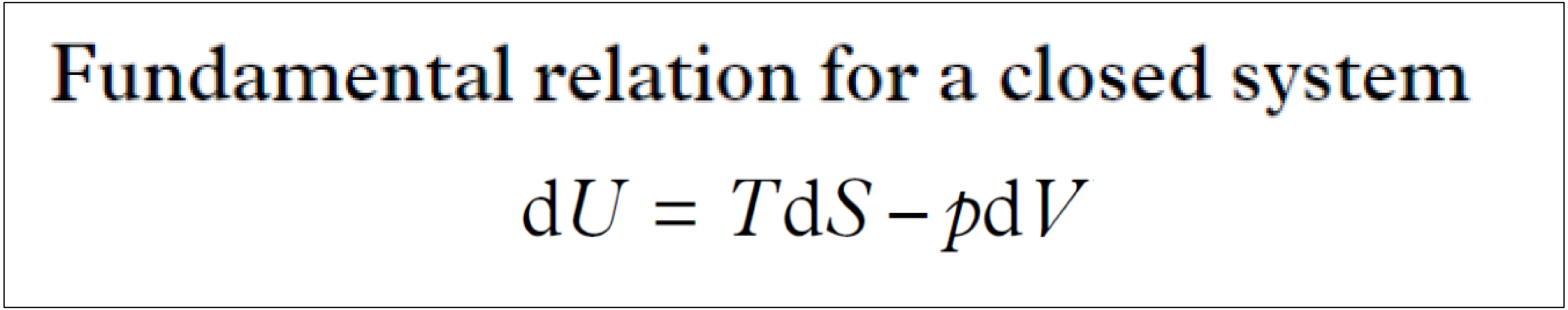
Clausius’s theorem The integral $\oint \text{đ}Q/T \leq 0$ for any closed cycle, where equality holds if and only if the cycle is reversible.

Definition of ENTROPY

A function of state, applicable to ANY thermodynamic system, whose value changes by

$$\mathrm{d}S = \frac{đQ_R}{T}$$

when heat $đQ_R$ passes into the system by a reversible heat transfer.



Fundamental relation for a closed system

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

{heat engine, second law} → Carnot theorem: $\eta \le \eta_R$

→ absolute temperature :

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}.$$

{heat ratio, Kelvin statement} → Clausius theorem:

$$\begin{cases} \oint \frac{đQ}{T} \le 0 \\ \oint \frac{đQ_R}{T} = 0 \end{cases}$$

→ ∃ entropy!, $\mathrm{d}S = \frac{đQ_\mathrm{R}}{T}.$

Fundamental relation for a closed system

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$