Thermodynamics lecture 4.

W.A.L.T. *Mostly clever examples of reasoning*

1. Adiabatic expansion; pV^{γ}
2. Carnot cycle
3. Clausius and Kelvin statements imply one another
4. Carnot’s theorem: efficiency of reversible heat engines
5. The definition of absolute temperature
6. Clausius’ theorem
7. → ENTROPY!

How to calculate in thermodynamics

(1) Identify clearly the thermodynamic system to be treated.

(2) Identify the nature of the interaction with the surroundings, and hence the type of *process*.

(3) Use the equation of state to gain information about initial and final conditions.

(4) At this stage you may well be able to calculate the heat and work inputs to the system, in terms of the state variables, although there may be some unknowns remaining in your expressions.

(5) If there remain some unknowns, use information about the heat capacity or the energy equation or both.

Adiabatic (i.e. reversible adiathermal) expansion of ideal gas

For:

- ideal gas
- with constant heat capacities

find: pV^{γ} = constant during an adiabatic change

where $\gamma \equiv \dfrac{C_p}{C_V}$ ("adiabatic index")

Example

(i) Explain carefully why, when gas leaks slowly out of a chamber, the expansion of the gas remaining in the chamber may be expected to be adiabatic (that is, quasistatic and without heat exchange). [Hint: choose carefully the physical system you wish to consider.]

(ii) A gas with $\gamma = 5/3$ leaks out of a chamber. If the initial pressure is $32p_0$ and the final pressure is p_0, show that the temperature falls by a factor 4, and that 1/8 of the particles remain in the chamber.

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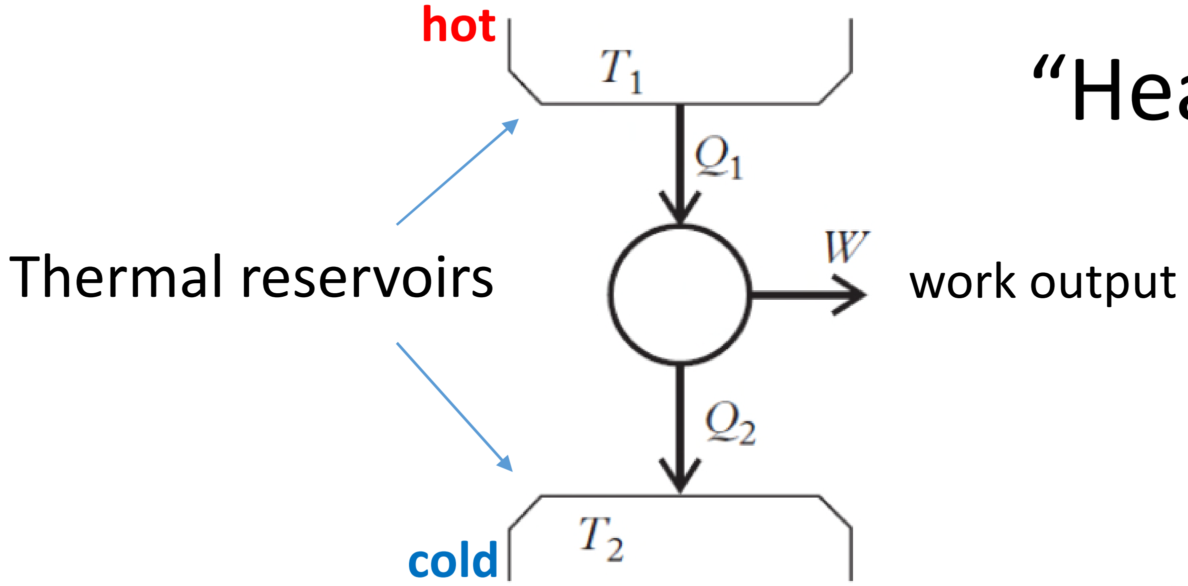
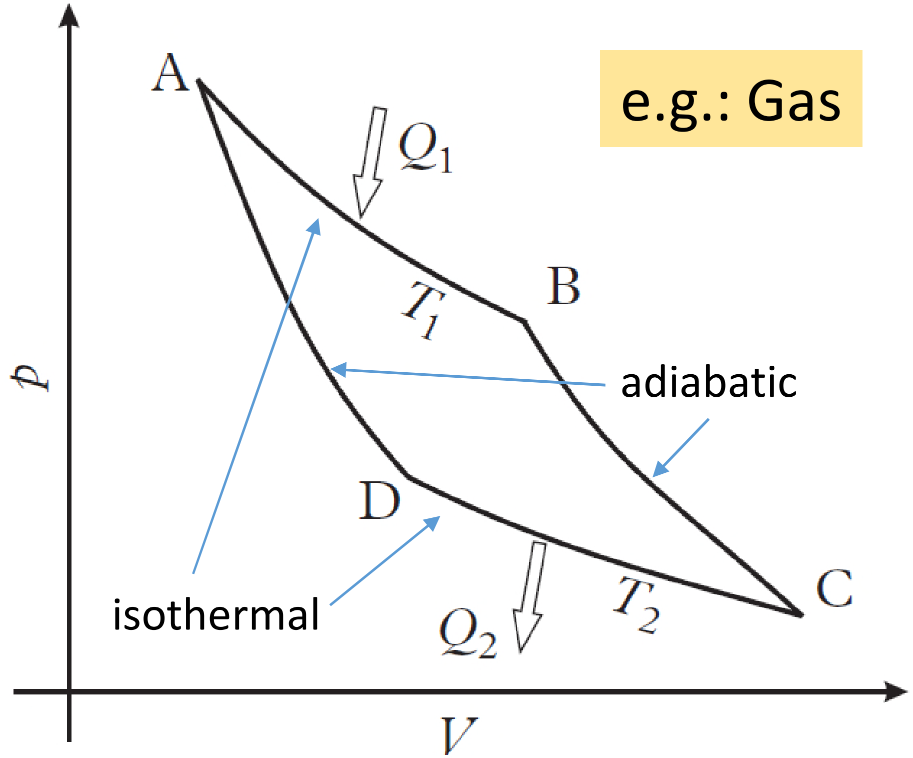
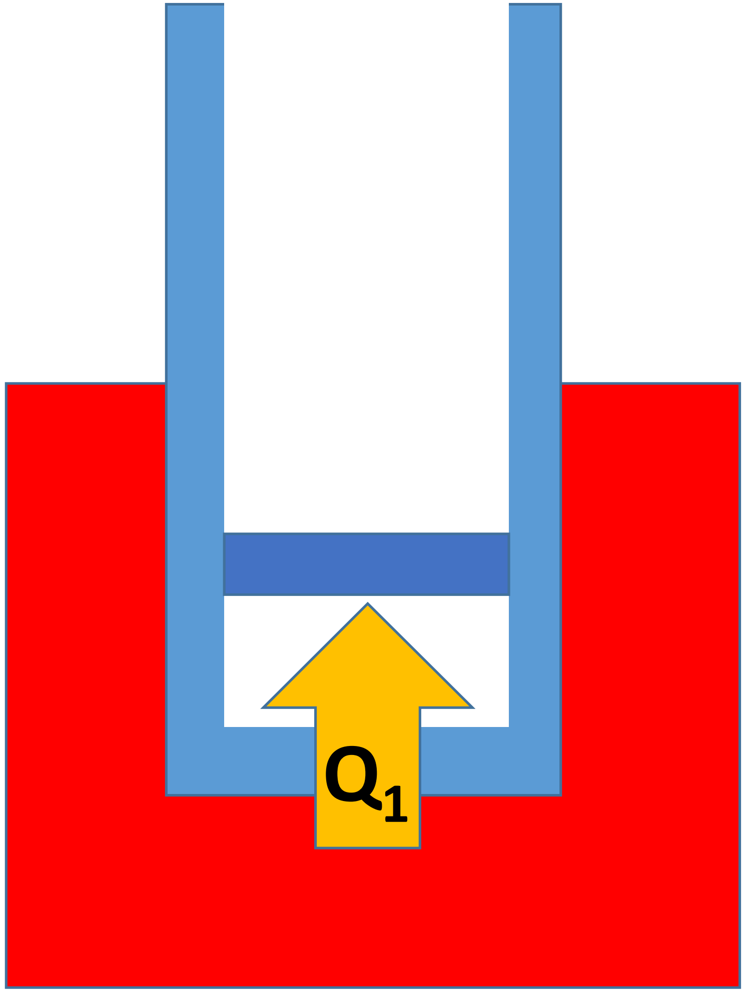
“Heat engine”

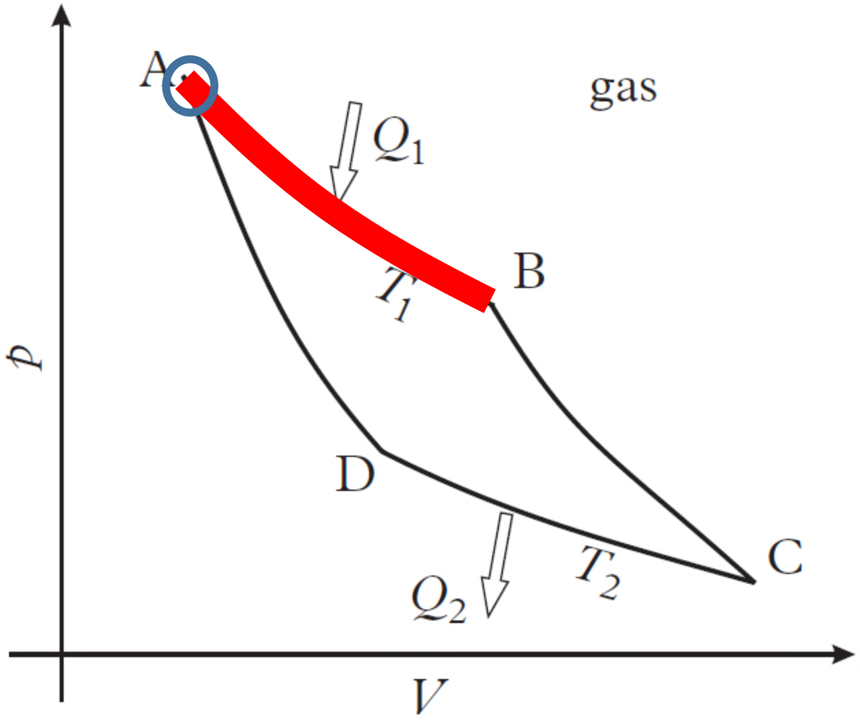


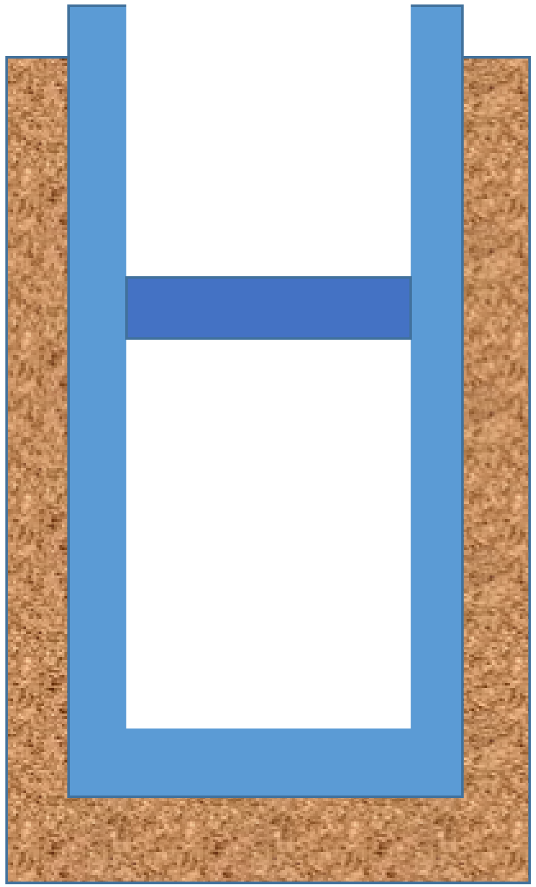


Carnot cycle:
2 adiabatic and
2 isothermal stages

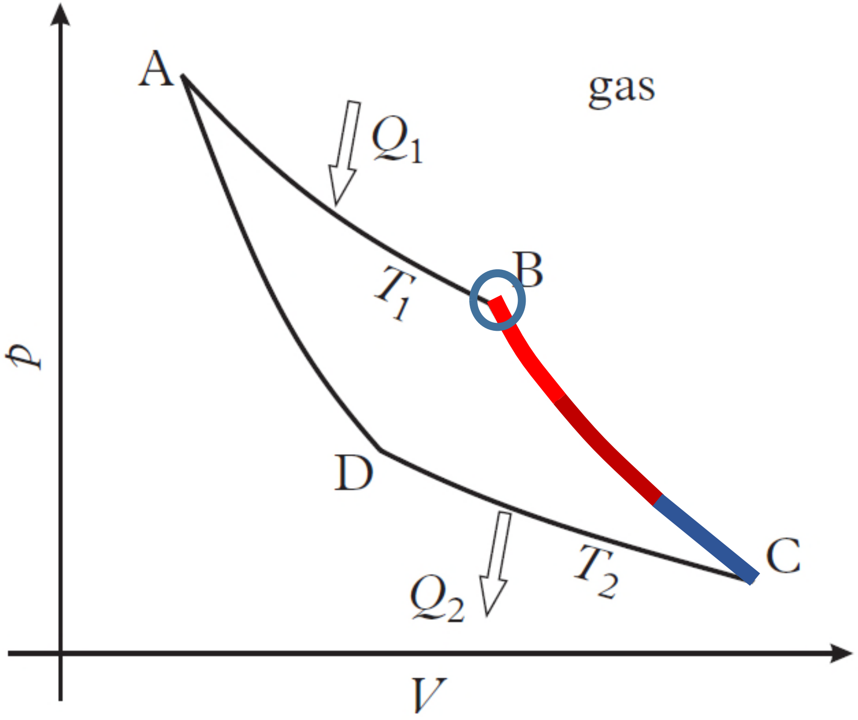
1. Thermal contact between the container and hot reservoir;
   allow the fluid to expand.



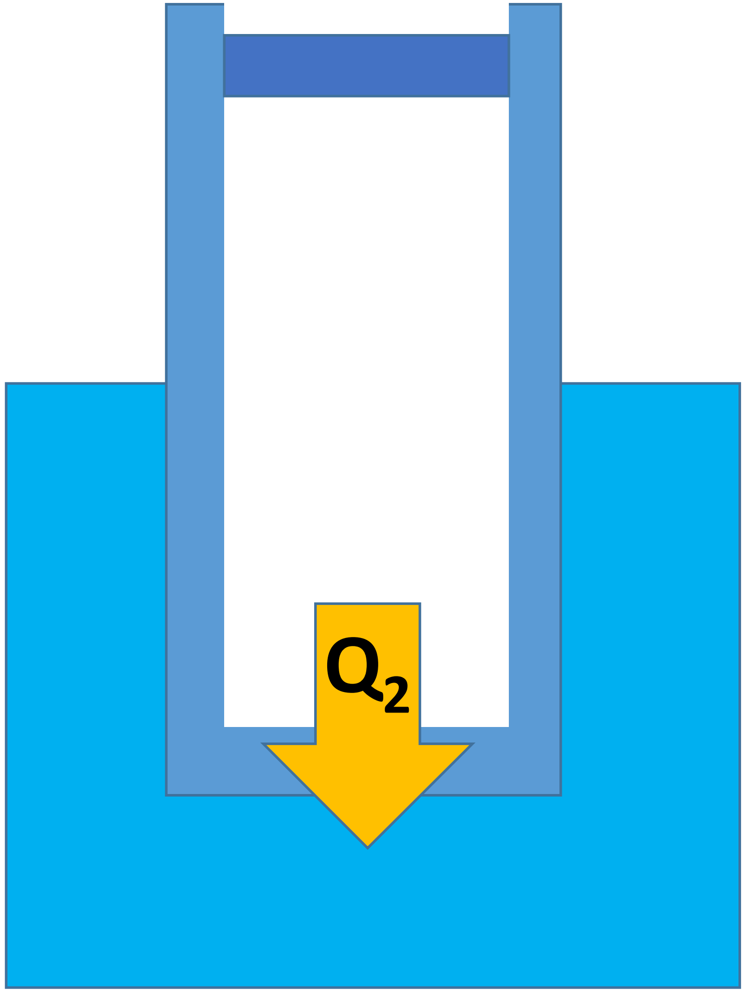


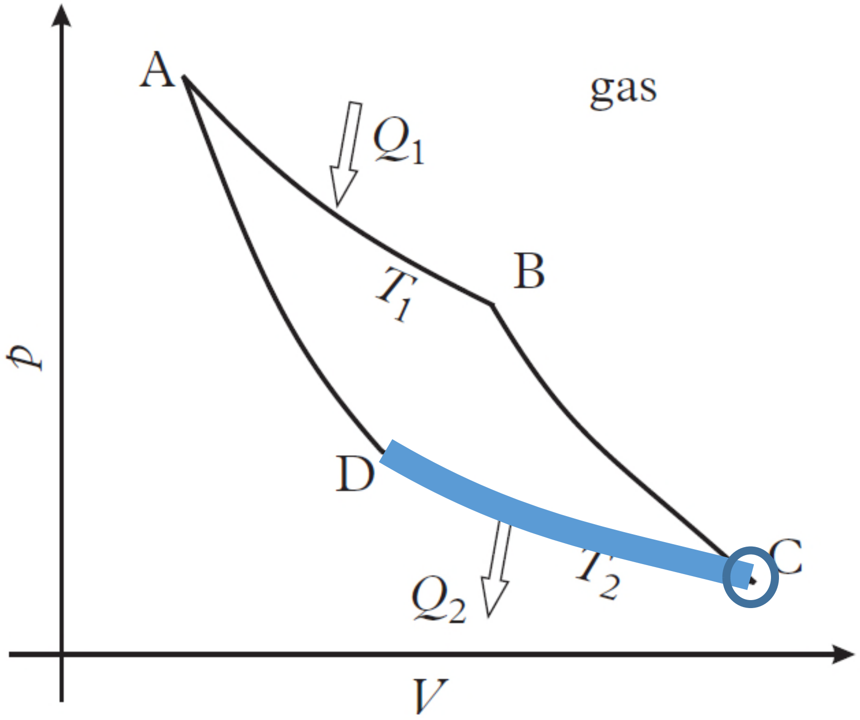


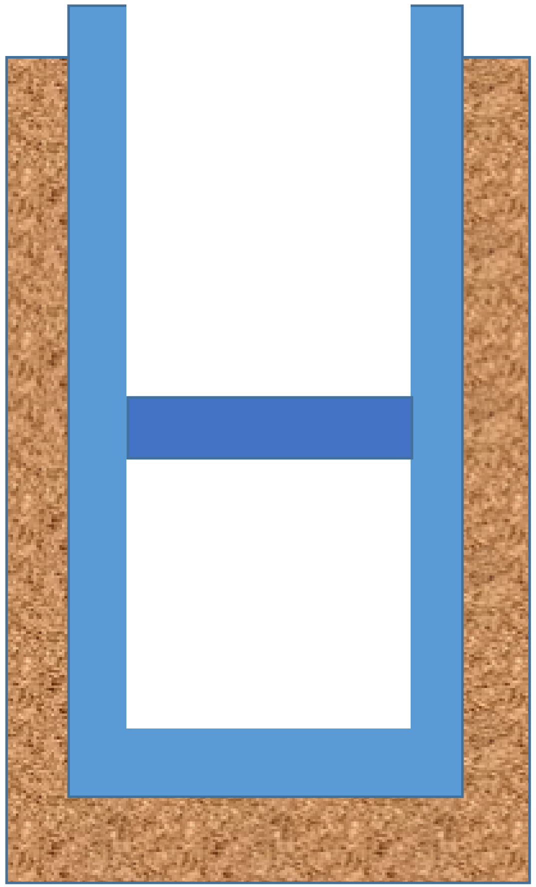
2. Thermally isolate the fluid and have it expand some more (so the fluid cools down).



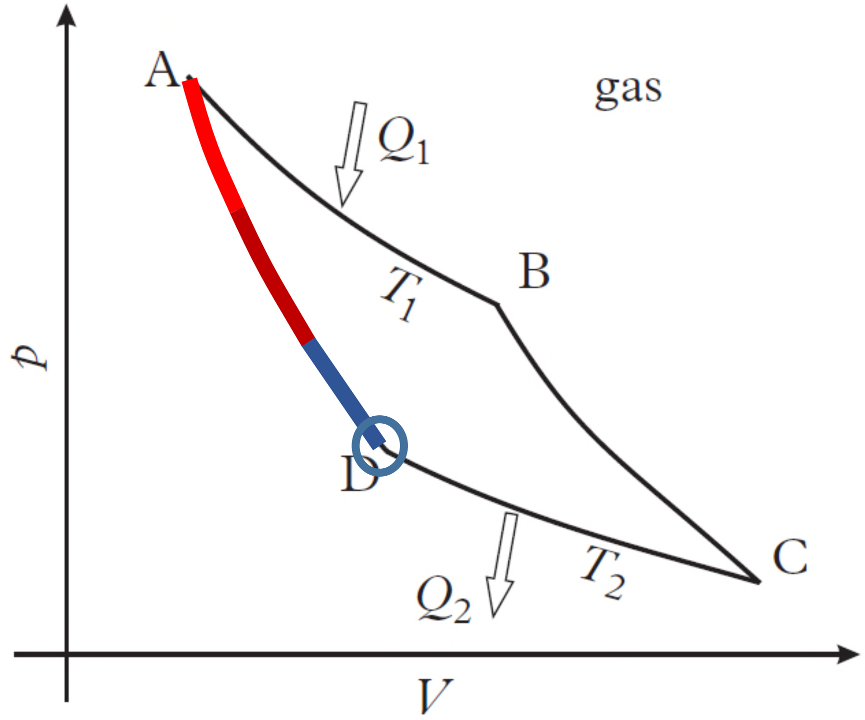
3. Contact the container with a cold reservoir and compress the fluid (the reservoir keeps it cool).

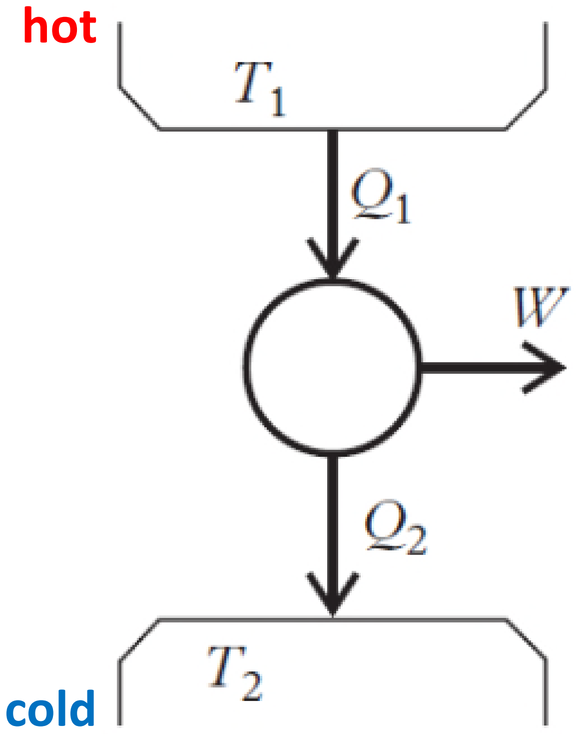




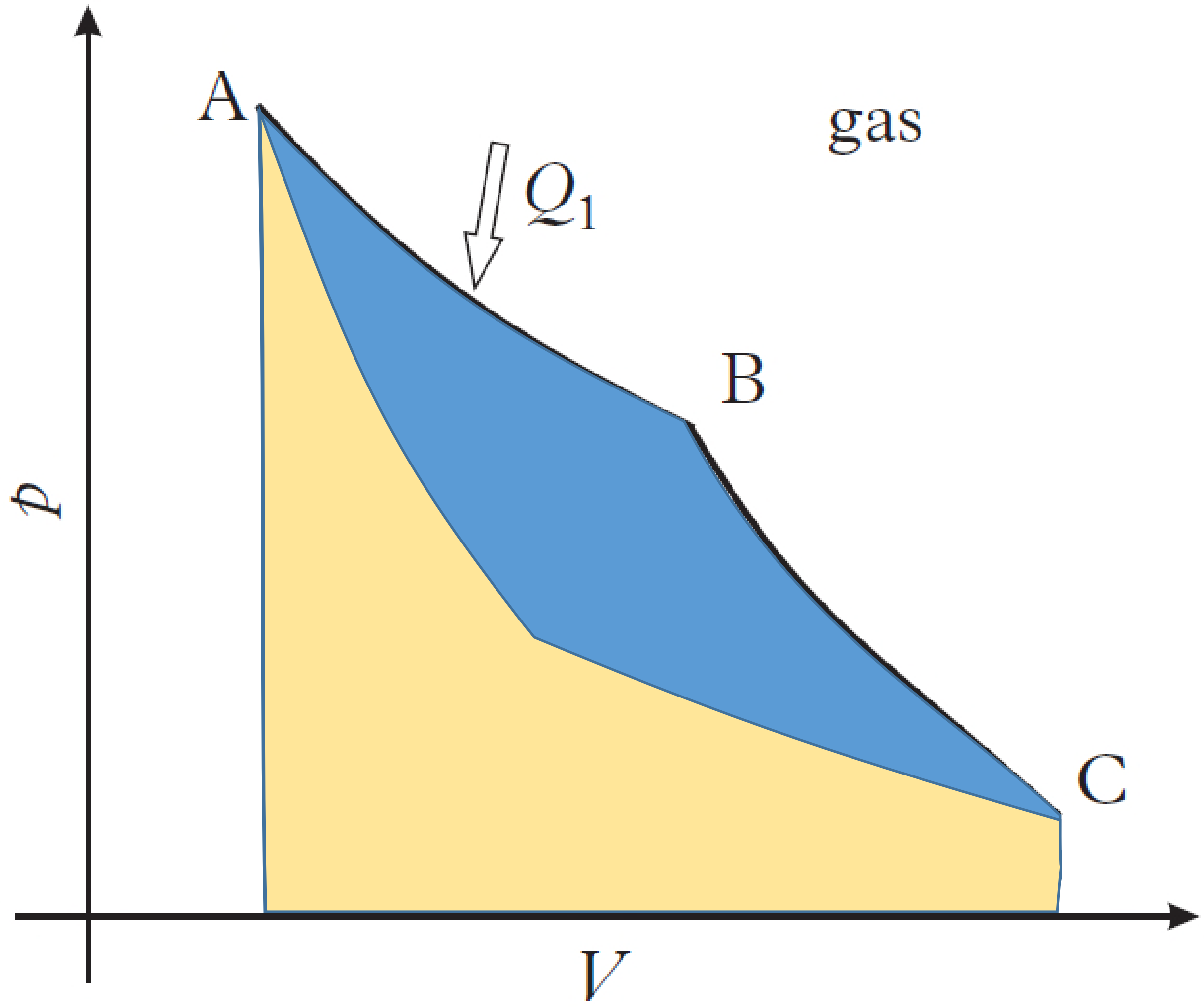


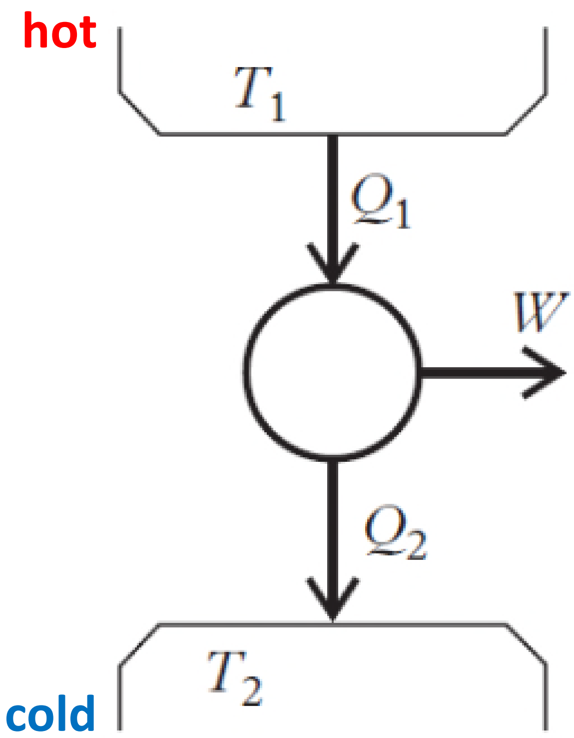
4. Thermally isolate the fluid and compress it some more (so it gets hotter).



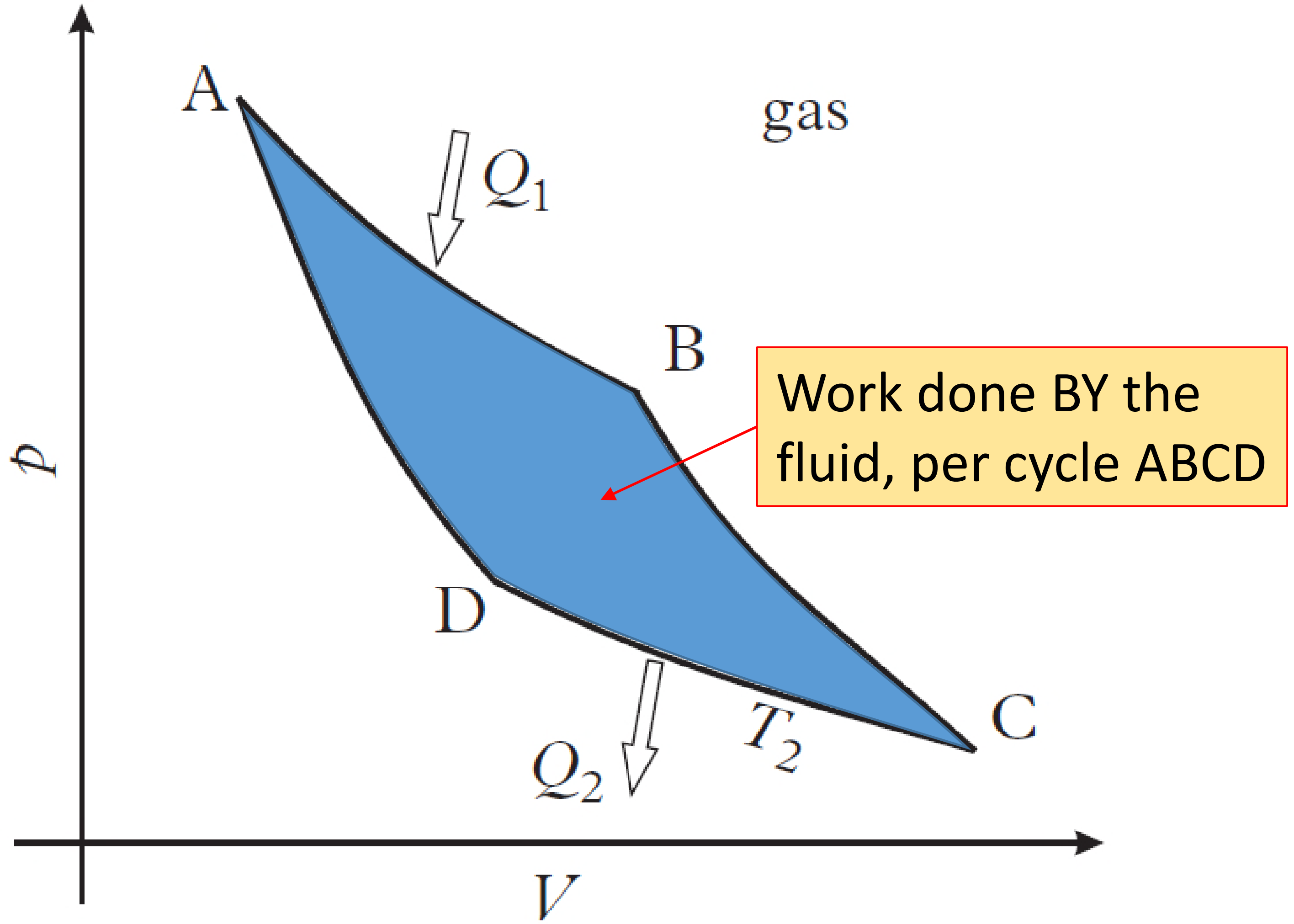


$$W = Q_1 - Q_2$$

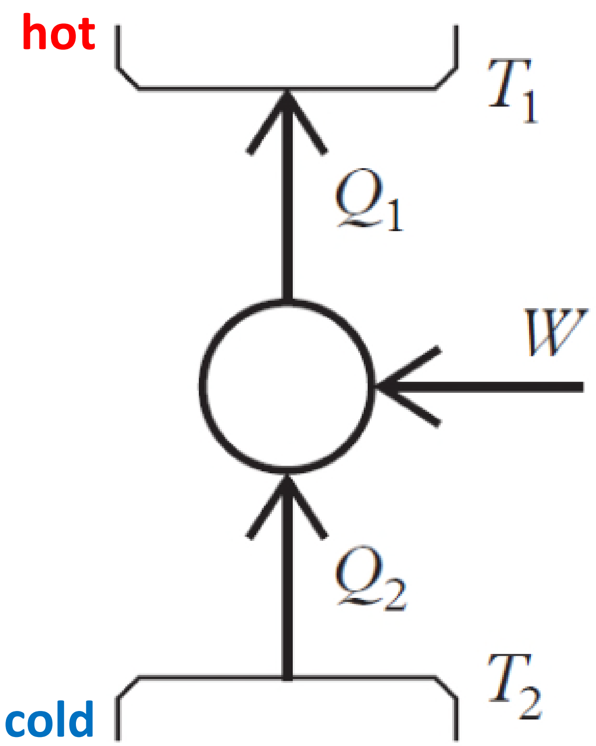



hot
T_1
Q_1
W
Q_2
T_2
cold

$$W = Q_1 - Q_2$$


A
gas
Q_1
B
Work done BY the fluid, per cycle ABCD
p
D
C
T_2
Q_2
V

We can run the same cycle in reverse:



Heat pump

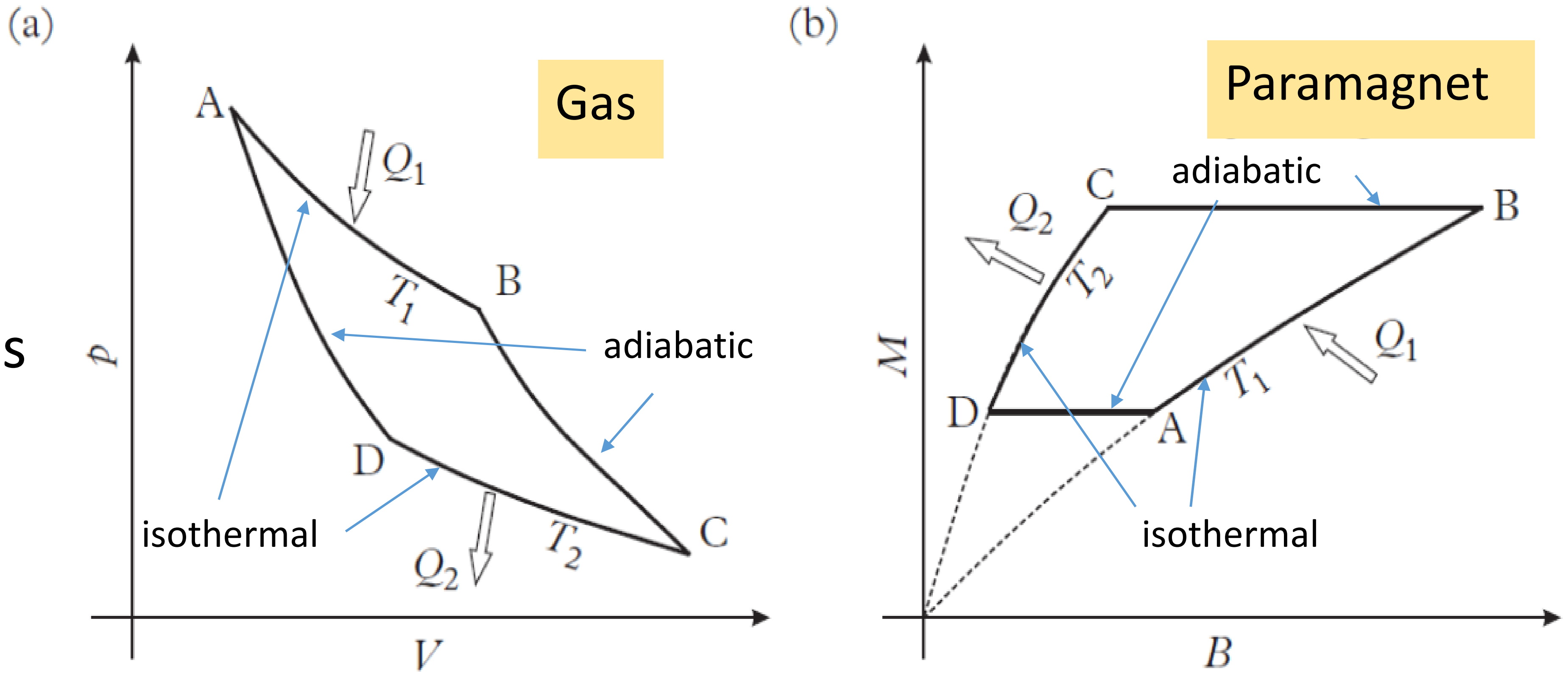
E.g.

- Refrigerator
- Air conditioning unit

Any type of system can have a Carnot cycle:

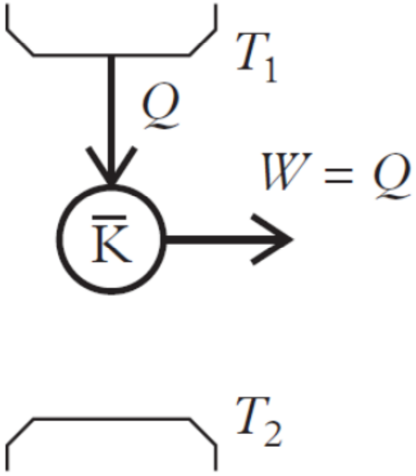
Solid / liquid / gas
Magnetic
Electric
Soap film
Etc.

Carnot cycle:
2 adiabatic and
2 isothermal stages

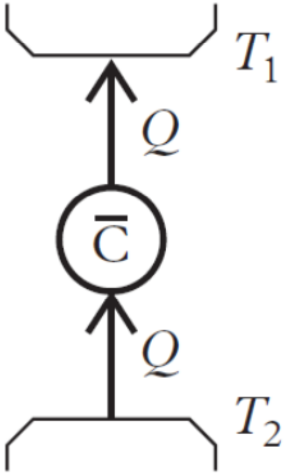


1. Adiabatic expansion; pV^{γ}
2. Carnot cycle
3. Clausius and Kelvin statements imply one another
4. Carnot's theorem: efficiency of reversible heat engines
5. The definition of absolute temperature
6. Clausius' theorem
7. → ENTROPY!

A beautifully elegant piece of reasoning



Forbidden by
Kelvin statement

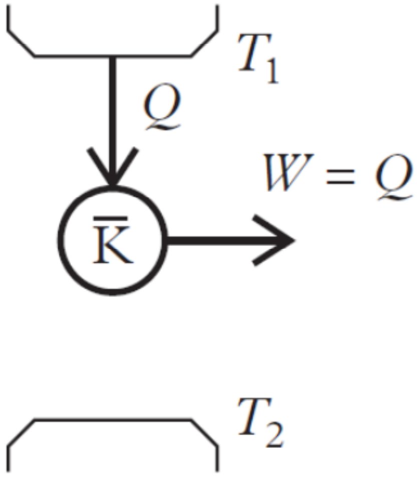


Forbidden by
Clausius statement

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

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.



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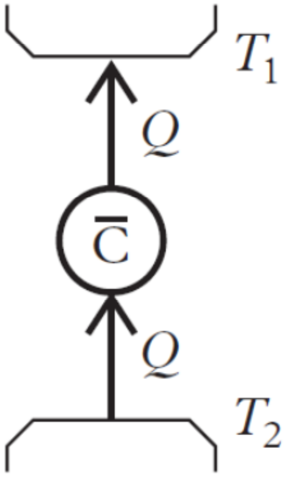
Kelvin statement



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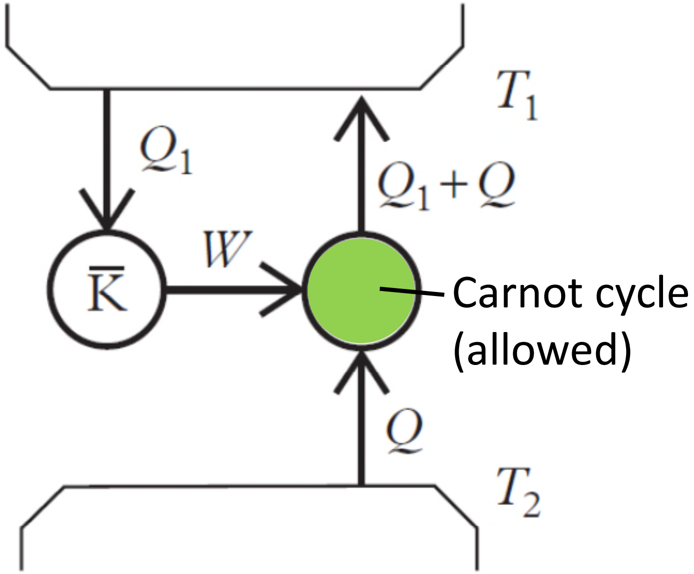
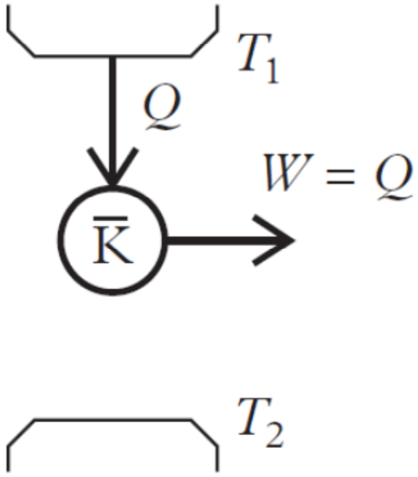
Clausius statement

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

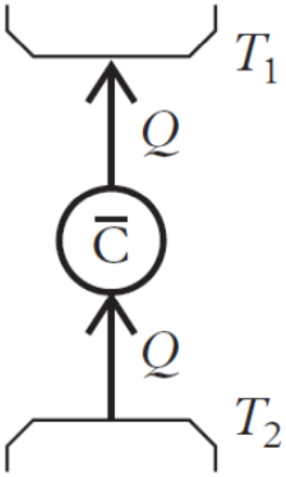


- Clausius statement of the 2nd Law says the net result here is physically impossible
- But we know the Carnot cycle is possible
- So the engine $\overline{\mathrm{K}}$ must be impossible
- … Which is the Kelvin statement of the 2nd Law

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

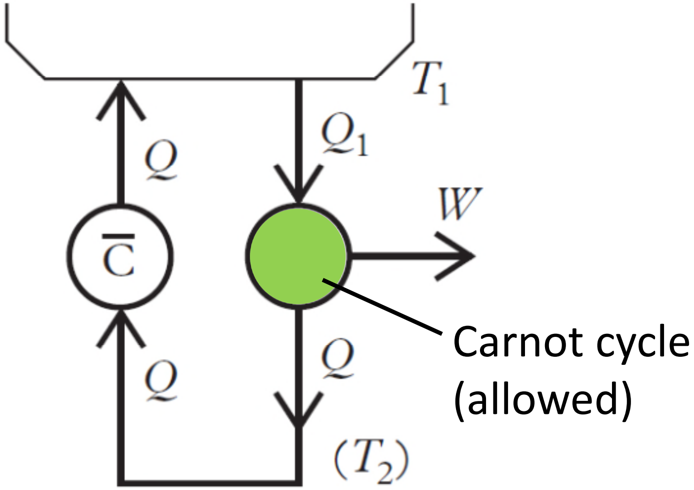


Forbidden by Kelvin statement



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 $\overline{C}$ must be impossible
- … Which is the Clausius statement of the 2nd Law



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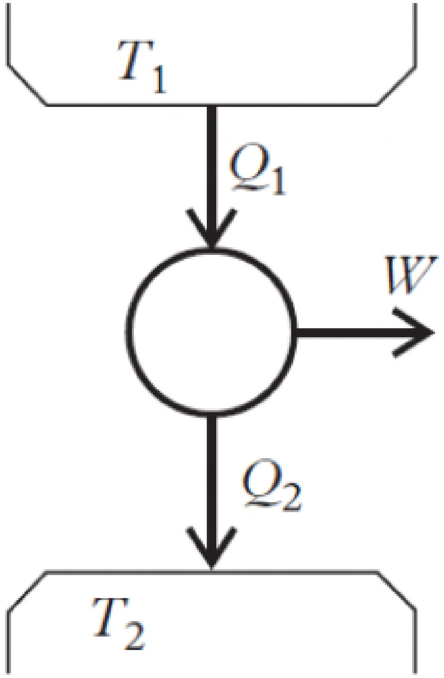
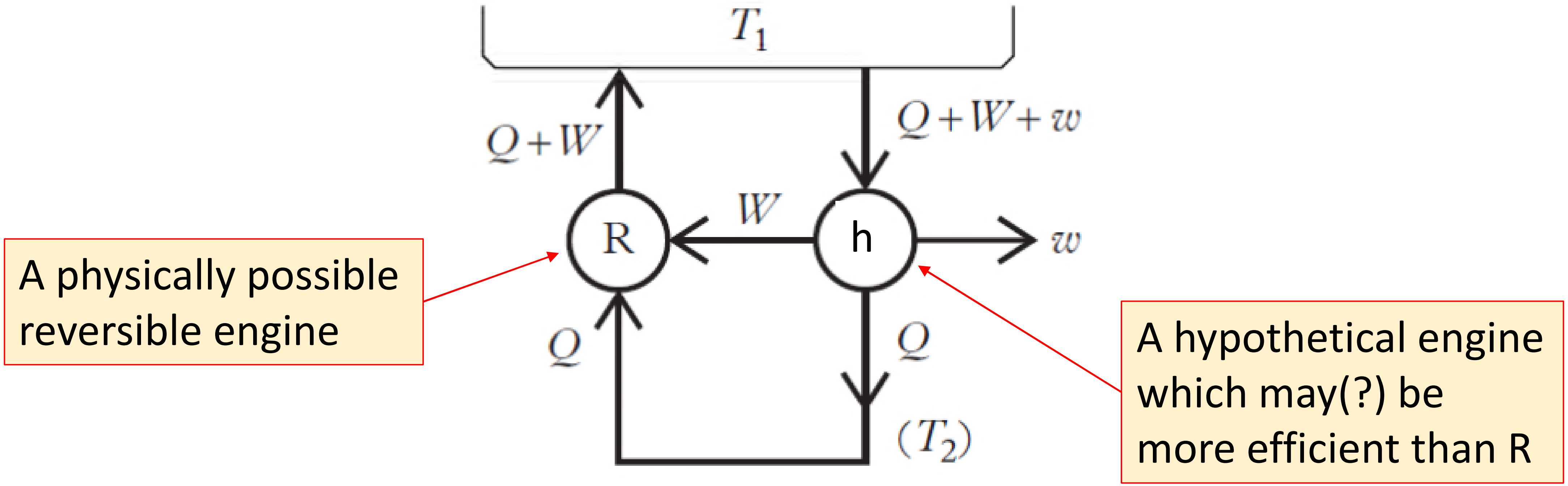
Definition of efficiency of a heat engine



$$W = Q_1 - Q_2$$

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

Carnot's theorem



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).

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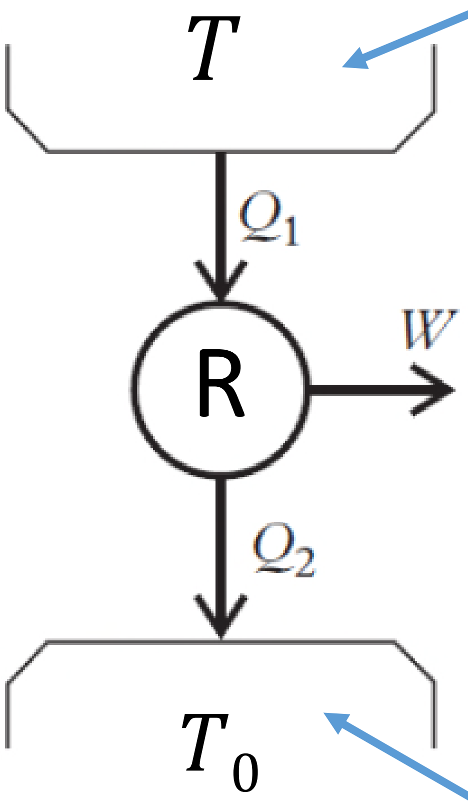
Clever definition.

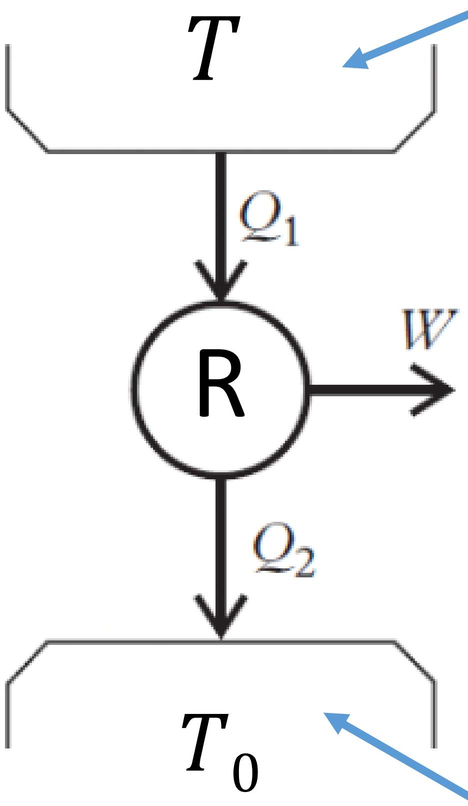
Definition of absolute temperature



Body in some arbitrary equilibrium state

A standard system in some chosen reference state
(e.g. 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



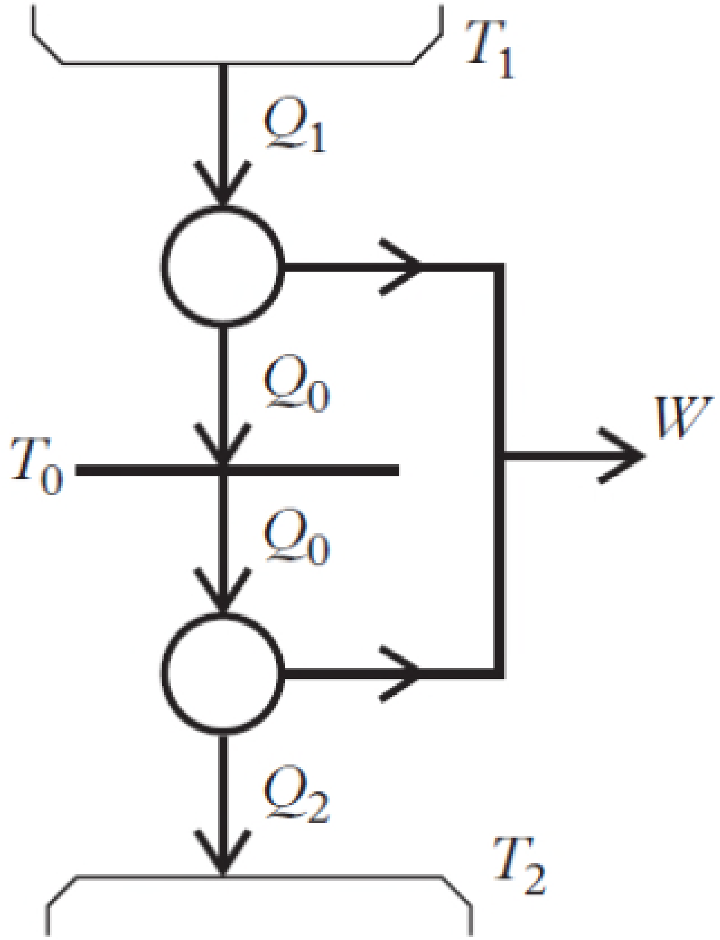
Body in some arbitrary equilibrium state

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

It works because all reversible engines have the same efficiency for given reservoirs.

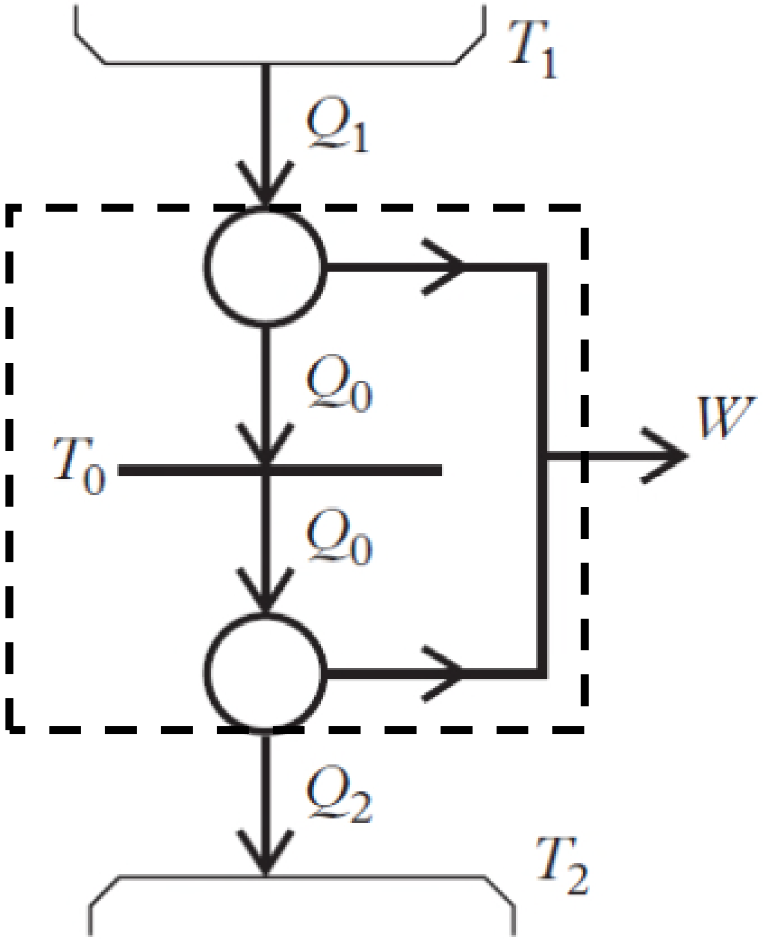
A standard system in some chosen reference state (e.g. pick pure water, ice, steam in mutual equilibrium; this is called the triple point of water).
Assign it some chosen temperature T_0 (e.g. 273.16 units)

Now consider any T_1, T_2 (not just the reference temperature)



Ratio of heats for a reversible engine

Now consider any T_1, T_2 (not just the reference temperature)



Ratio of heats for a reversible engine

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

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.

Thermodynamics lecture 4.

W.A.L.T.

1. Adiabatic expansion; pV^{γ}
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4. Carnot's theorem, efficiency of reversible heat engines
5. The definition of [illegible] temperature
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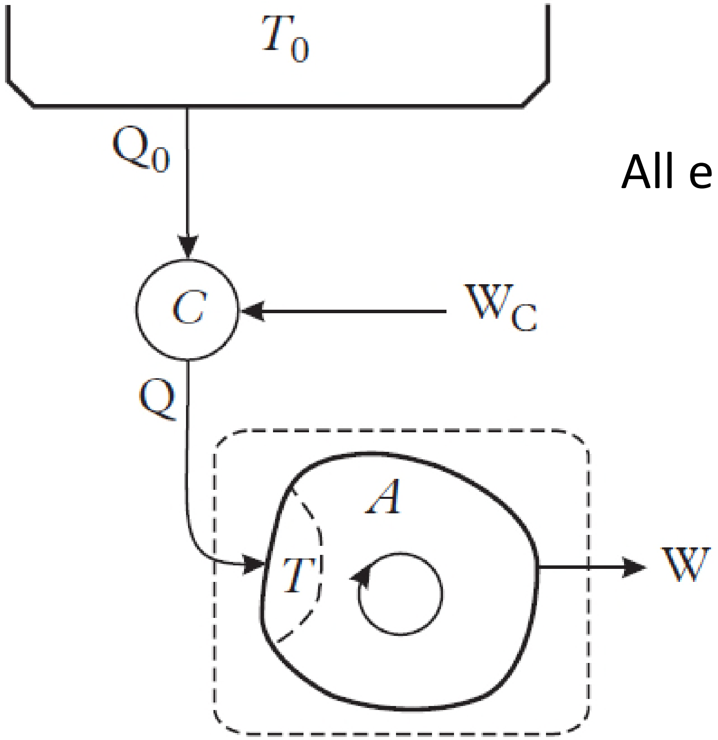
7. → ENTROPY!

An even more elegant piece of reasoning.

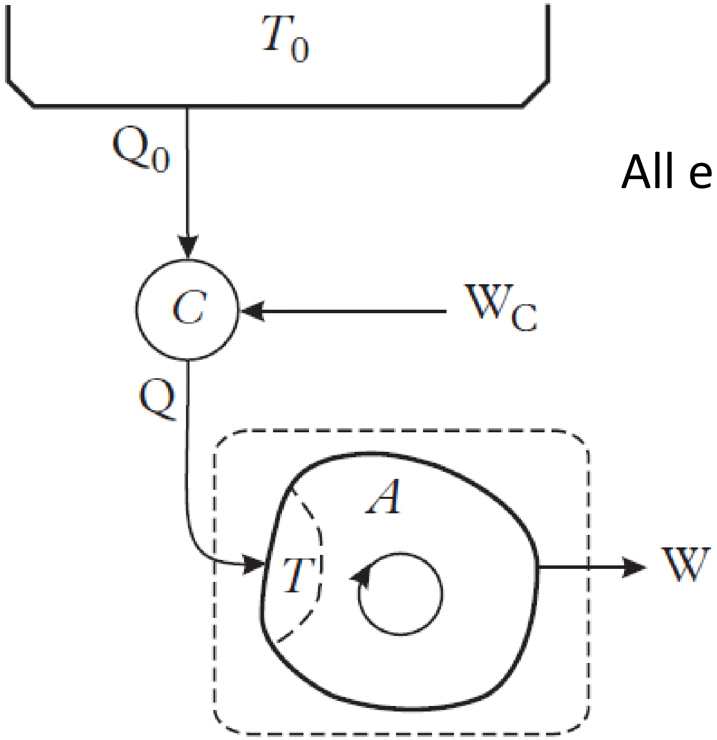


All entirely possible!

Per cycle:

Net heat supplied to system: $$Q = \oint đQ$$ Can be +ve or -ve

Net heat extracted from reservoir: $$Q_0 = \oint đQ_0 = T_0 \oint \frac{1}{T} đQ$$



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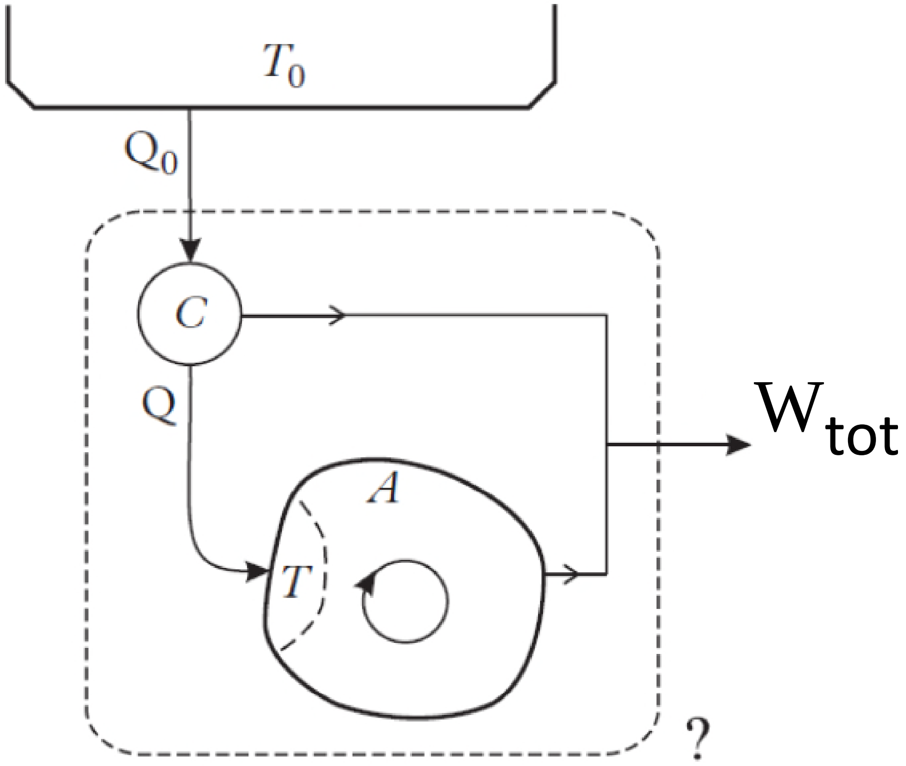


Per cycle:

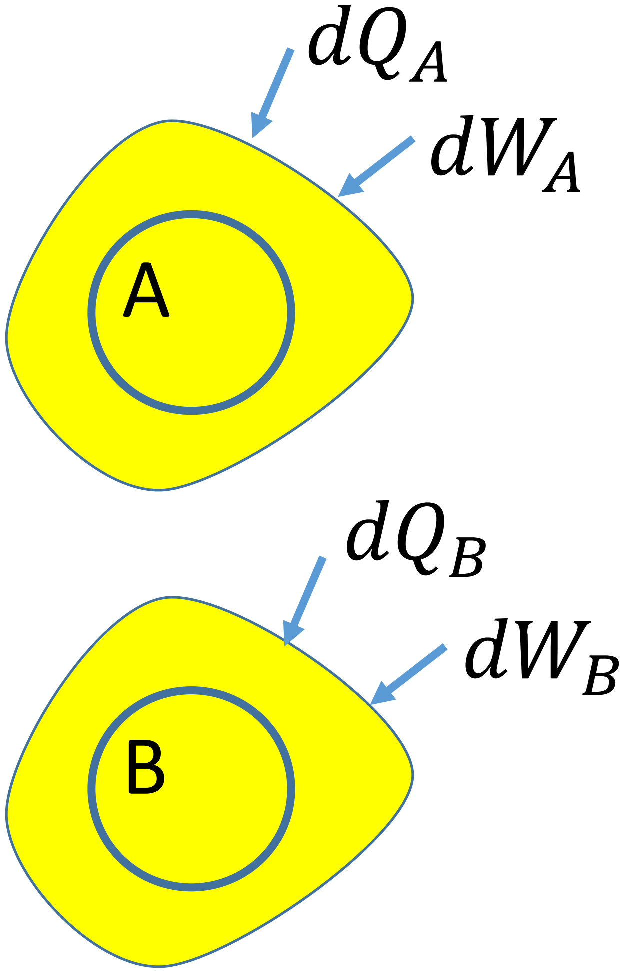
Net heat supplied to system: $$Q = \oint đQ$$ Can be +ve or -ve

Net heat extracted from reservoir: $$Q_0 = \oint đQ_0 = T_0 \oint \frac{1}{T} đQ \leq 0$$

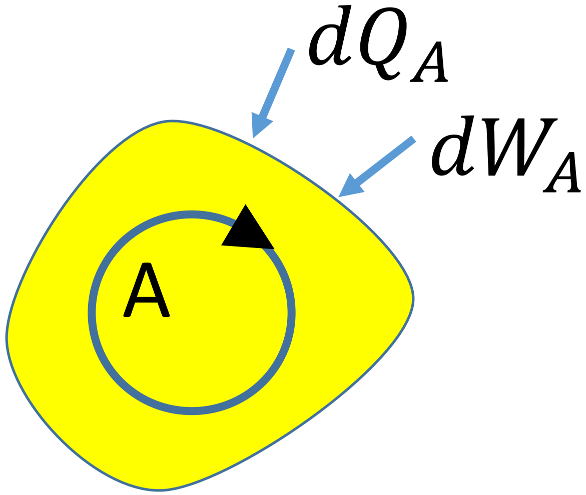
(Kelvin statement)

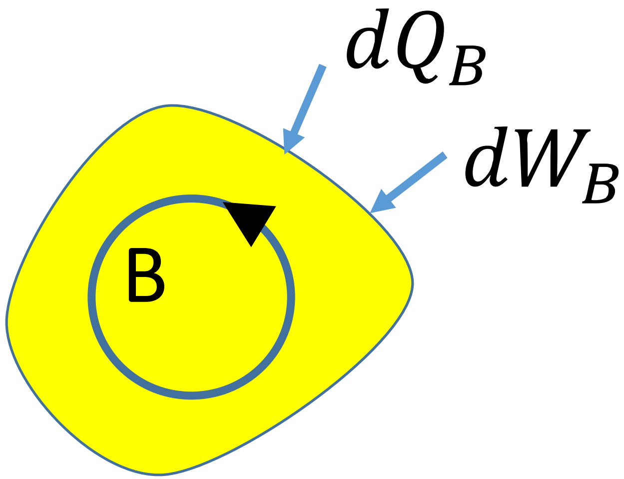
Clausius' theorem, first part

For any cycle: $$\oint \frac{1}{T} đQ \leq 0.$$



$$\left.\begin{array}{l}\oint \frac{\mathrm{d}Q_A}{T_A} \leq 0 \\ \oint \frac{\mathrm{d}Q_B}{T_B} \leq 0\end{array}\right\} \text{ for any processes } A,\ B.$$





$$\left.\begin{array}{l} \oint \frac{\mathrm{d}Q_A}{T_A} \le 0 \\ \oint \frac{\mathrm{d}Q_B}{T_B} \le 0 \end{array}\right\} \text{ for any processes } A,\, B.$$

But now suppose process B is the reverse of process A in all respects (only possible for reversible processes). In this case we will have, at each stage,

$$dQ_B = -dQ_A \qquad \text{and } T_B = T_A$$

so in this case the second result above can be written

$$\oint \frac{-\mathrm{d}Q_A}{T_A} \le 0.$$

But, for any x, if $x \le 0$ and $-x \le 0$ then $x = 0$. Therefore we must have

$$\oint \frac{\mathrm{d}Q_A}{T_A} = 0.$$

Conclusion: this integral is zero for any reversible process.

Clausius' theorem, in full:

Clausius's theorem The integral $\oint đQ/T \leq 0$ 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

$$dU = TdS - pdV$$

$\{\text{heat engine, second law}\} \rightarrow$ Carnot theorem: $\eta \leq \eta_R$

$\rightarrow$ absolute temperature :

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

$\{\text{heat ratio, Kelvin statement}\} \rightarrow$ Clausius theorem:

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

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

Fundamental relation for a closed system

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