

04. Thermodynamic Entropy and Information

- Recall:

Fisher Information

$$I_{\text{Fisher}}(p; \theta) = - \int \left(\frac{\partial^2}{\partial \theta^2} \log p(x; \theta) \right) p(x; \theta) dx$$

- The average value of the sensitivity $-\frac{\partial^2}{\partial \theta^2} \log p(x; \theta)$ of a probability distribution $p(x; \theta)$ to θ .
- How spread out p is with respect to θ .

Shannon entropy

$$S_{\text{Shan}}(p) = - \int (\log_2 p(x)) p(x) dx$$

- The average value of the Shannon information content $-\log_2 p(x)$ of a probability distribution $p(x)$.
- How spread out p is.



What does this have to do with "entropy"?

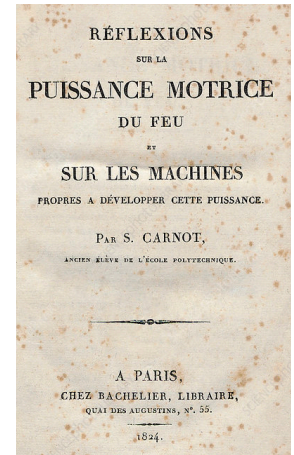
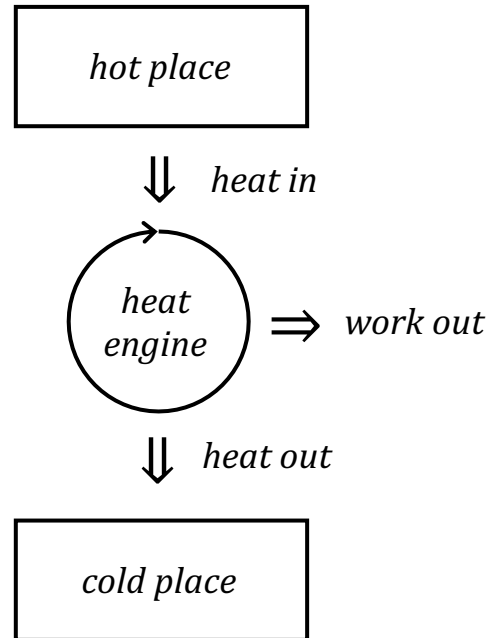
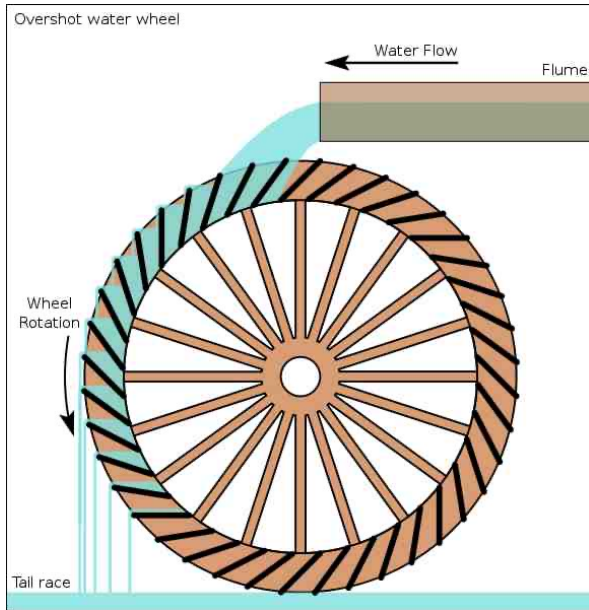
Let's go back to the source...

1. Heat Engines

- Idea: Treat heat in analogy with water as a substance that produces work when it "falls" from a hot place to a cold place.



Sadi Carnot
(1796-1832)

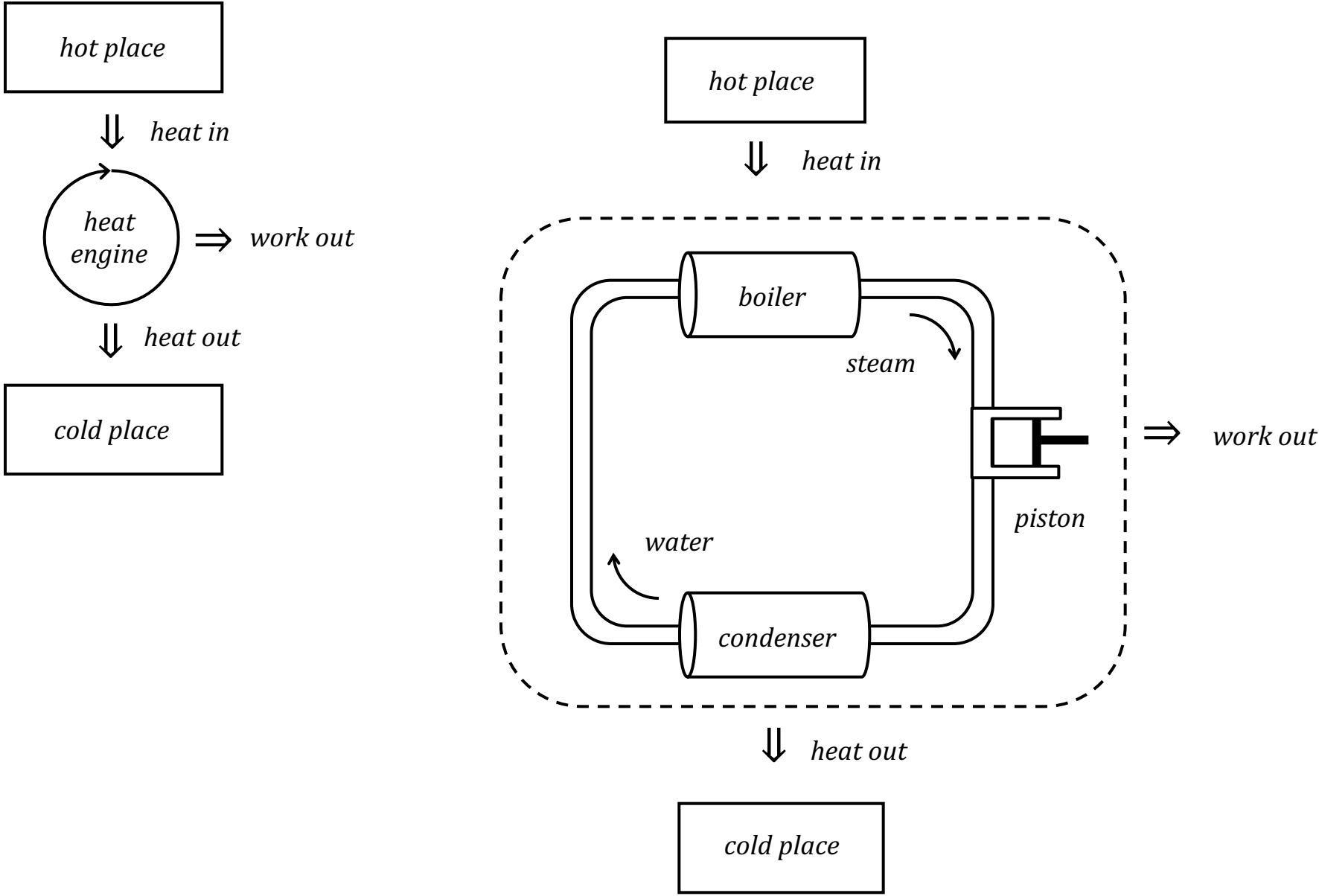


Carnot, S. (1824) "Reflections on the Motive Power of Fire"

Heat Engine

Cyclic process in which work is produced by the fall of heat from a hot place to a cold place.

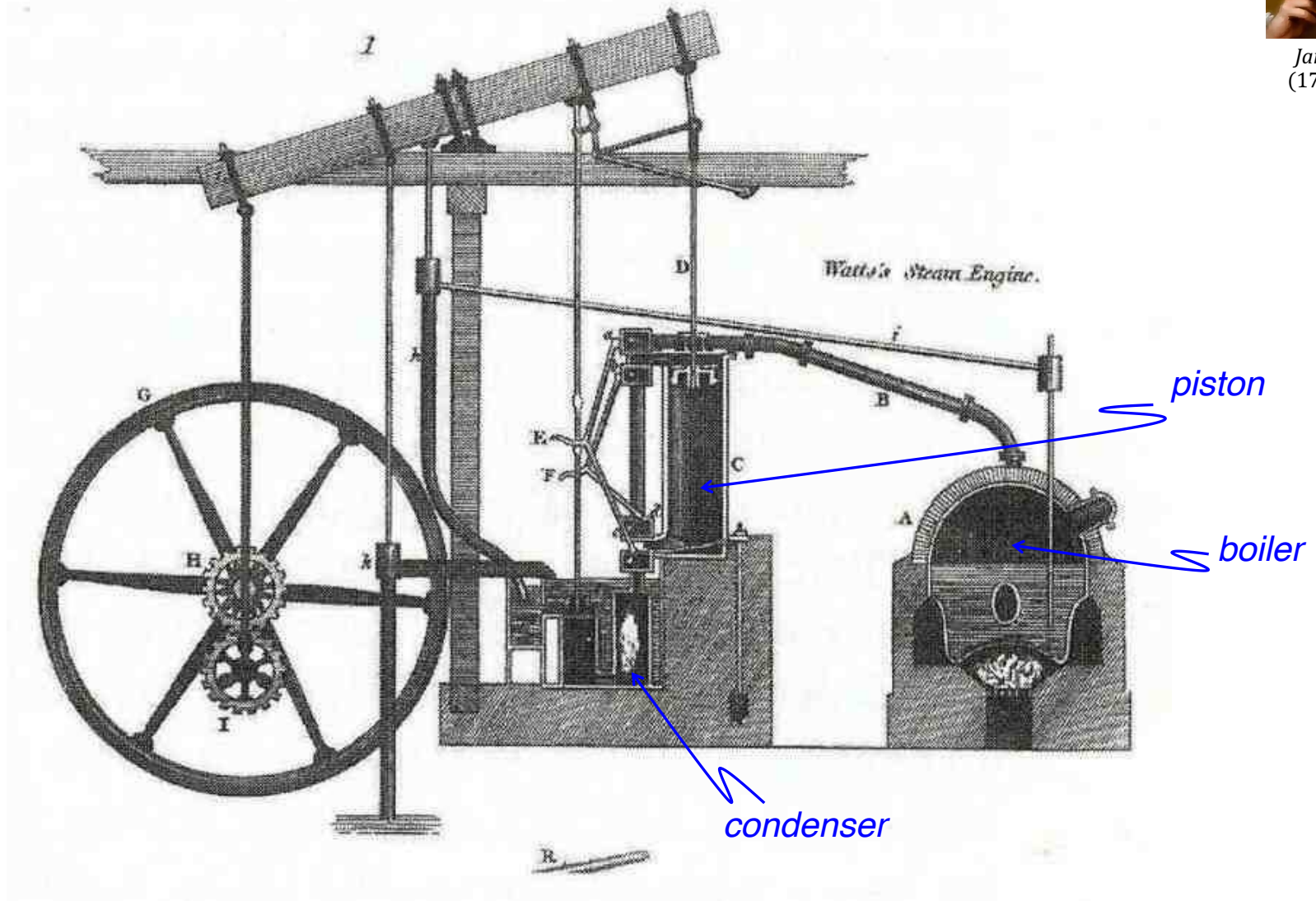
- Heat engine of economic interest in 1800s: Steam engine!



- James Watt (1765): Improvement in efficiency of Newcomen steam engine (addition of external condenser).



James Watt
(1736-1819)



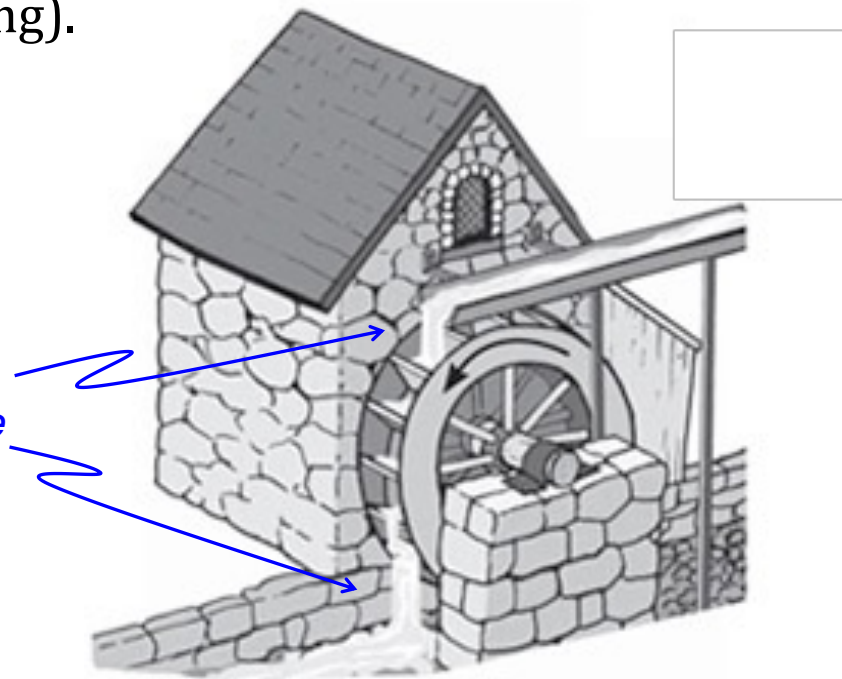
- Important question: What is the *maximally efficient* heat engine (*i.e.*, maximizes work output while minimizing waste)?

Maximum efficiency requires the heat-flow between hot place and engine, and engine and cold place, to occur at *equal temperatures*.



- Analogy with water-wheel: Maximum efficiency requires water-flow between stream and water-wheel to occur at *equal heights* (minimizes splashing).

*minimize splashing at
high flume and low flume*



Carnot Cycle = One complete cycle of a maximally efficient heat engine.

- Gas in cylinder with piston undergoing transitions between equilibrium states.
- Analogy: temperature $\approx$ height, heat $\approx$ water

1→2: Isothermal expansion

- Heat absorbed at constant temp.
- Gas expands, doing work.

2→3: Adiabatic expansion

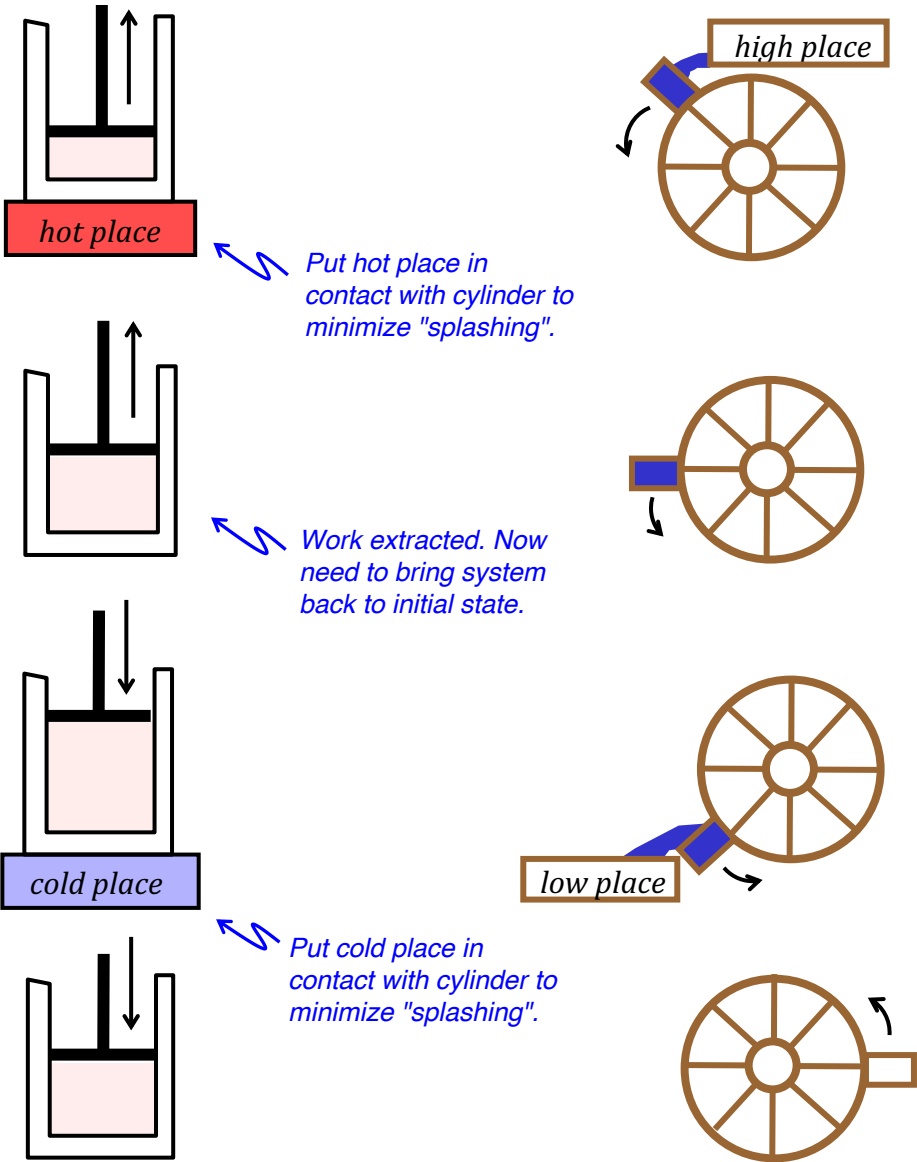
- Temp decreases at constant heat.
- Gas expands, doing work.

3→4: Isothermal contraction

- Heat exhausted at constant temp.
- Gas contracts, work done on it.

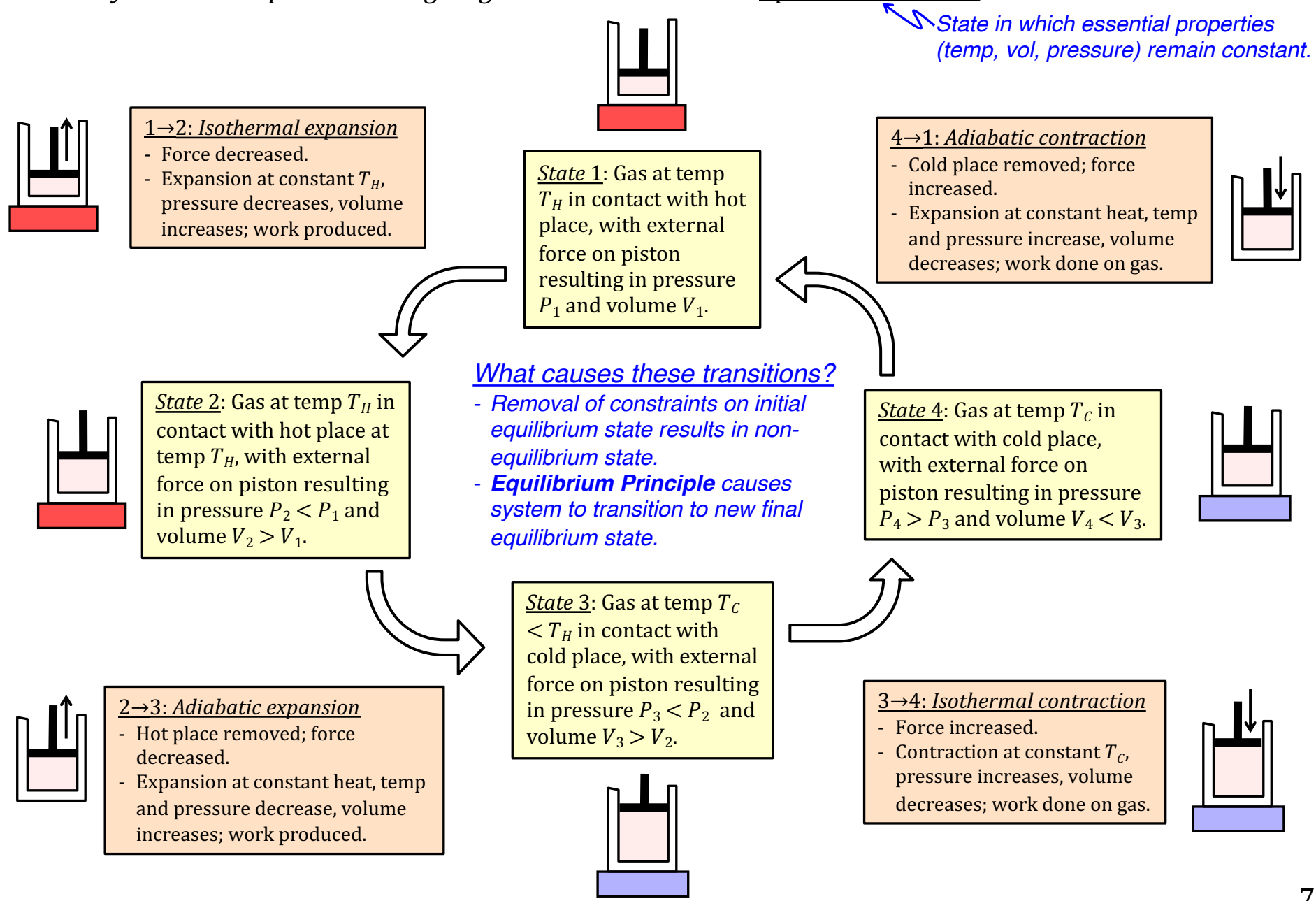
4→1: Adiabatic contraction

- Temp increases at constant heat.
- Gas contracts, work done on it.



Carnot Cycle = One complete cycle of a maximally efficient heat engine.

- Gas in cylinder with piston undergoing transitions between equilibrium states.



The "approach to equilibrium"

Equilibrium Principle

An isolated system in an arbitrary initial state will spontaneously attain a unique state of equilibrium.

Not the same as the 2nd Law (as we will see)!

An empirical observation:

"The most basic empirical principle is that macroscopic bodies when left to themselves, i.e. when isolated from an environment, eventually settle down in an equilibrium state in which no further observable changes occur.

Moreover, for simple, homogeneous bodies, this equilibrium state is fully characterized by the values of a small number of macroscopic variables."*

*Uffink, J. (2007) "Compendium of the Foundations of Classical Statistical Physics", in Earman, J. & J. Butterfield (eds.) *Handbook of the Philosophy of Science: Philosophy of Physics*, Elsevier, pp. 923-1074.

2. Second Law: Clausius and Thomson Versions

Additional Claims about Heat Engines

Claim 1. The maximum efficiency (work done per heat input) of any heat engine is equal to that of a reversible heat engine operating between the same hot and cold places.

Claim 2. The efficiency of any heat engine, reversible or irreversible, only depends on the *temperature* of the hot and cold places; *not* on the working fluid.



Claim 1. The maximum efficiency of any heat engine is equal to that of a reversible engine operating between the same hot and cold places.

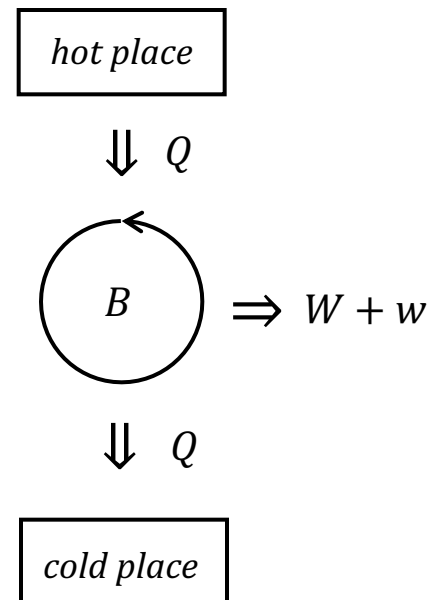
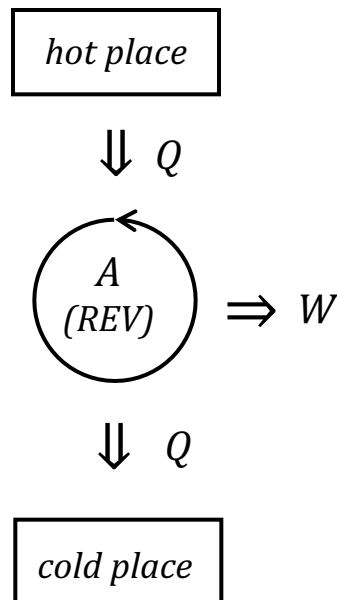
Proof #1:

- Suppose we have a reversible engine A that produces work W .
- Suppose there is a more efficient engine B between the same hot and cold places (B uses the same heat as A and produces more work).
- Now reverse A and hook it up to B .



William Thomson
(1824-1907)

Thomson, W. (1849)
"An Account of Carnot's
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Claim 1. The maximum efficiency of any heat engine is equal to that of a reversible engine operating between the same hot and cold places.

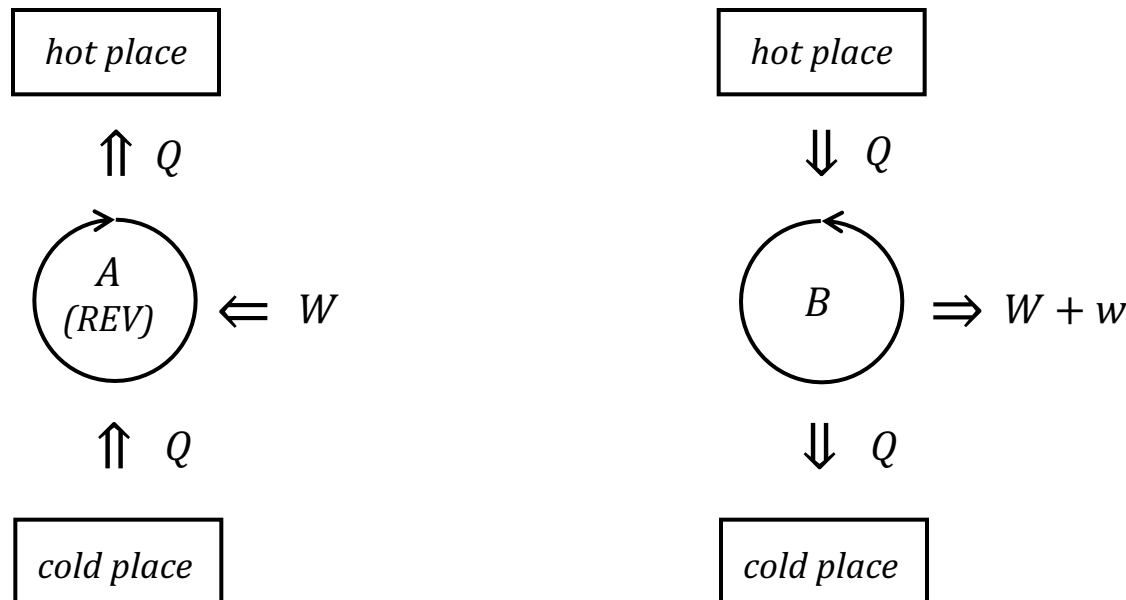
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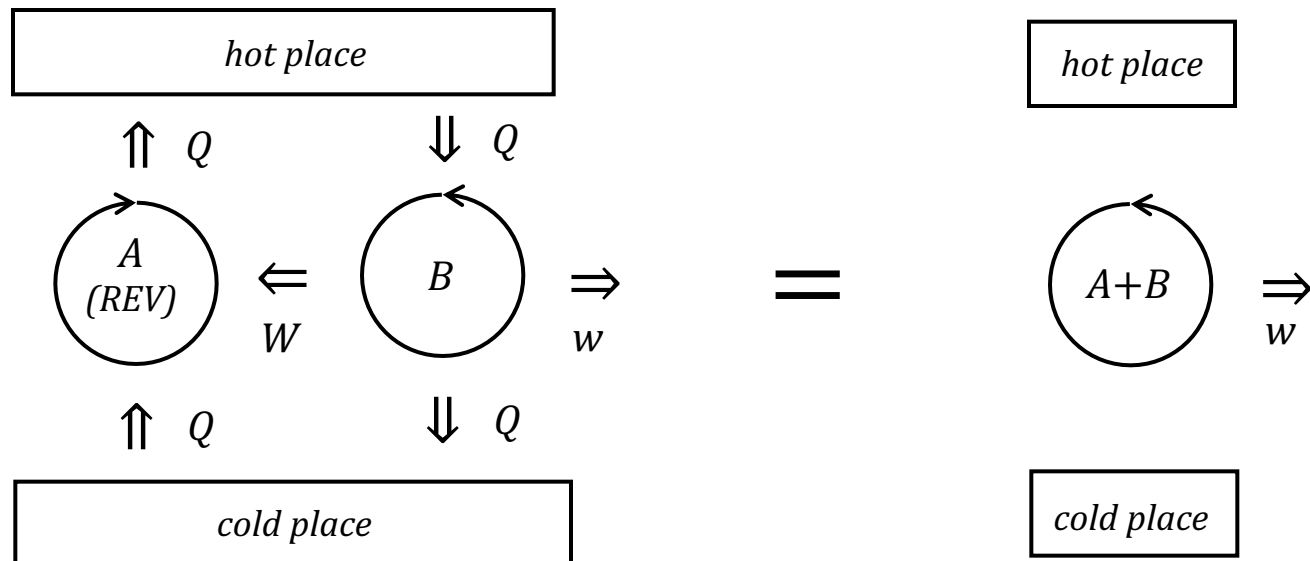
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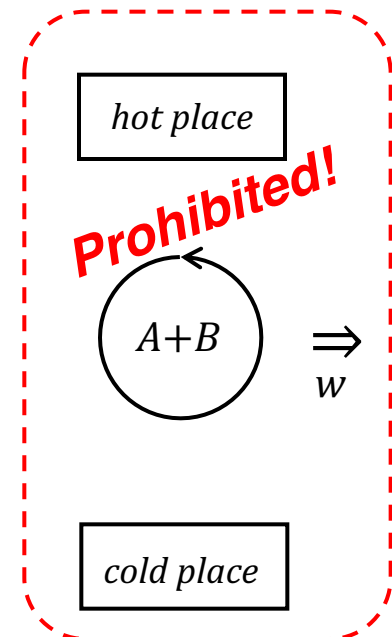
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Carnot: This is impossible!



"...this would be not only perpetual motion, but an unlimited creation of motive power... Such a creation is entirely contrary to ideas now accepted, to the laws of mechanics and of sound physics. It is inadmissible."



Claim 1. The maximum efficiency of any heat engine is equal to that of a reversible engine operating between the same hot and cold places.

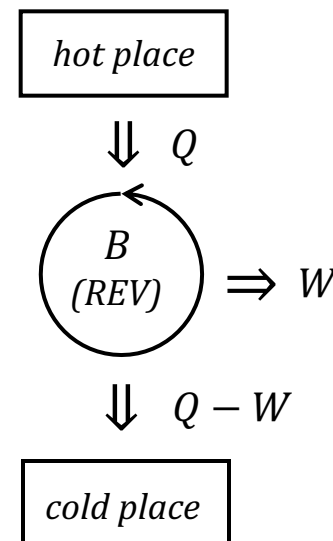
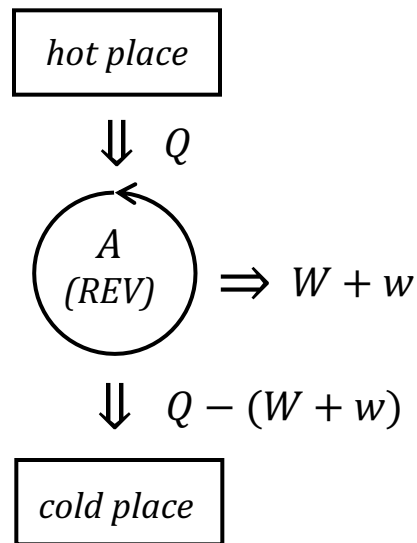
Proof #2:

- Let A and B be reversible engines with same hot and cold places, and let A be more efficient (in the sense that A produces more work than B for the same heat in).
- Reverse B and hook it up to A .



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New hypothesis (Joule):
Heat and work are
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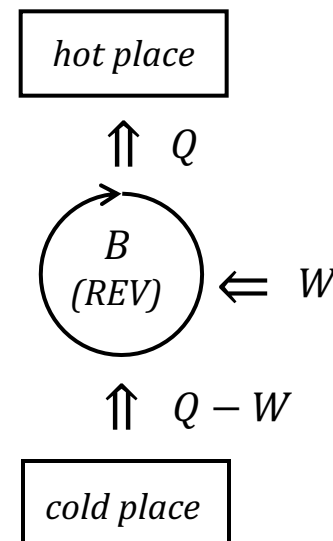
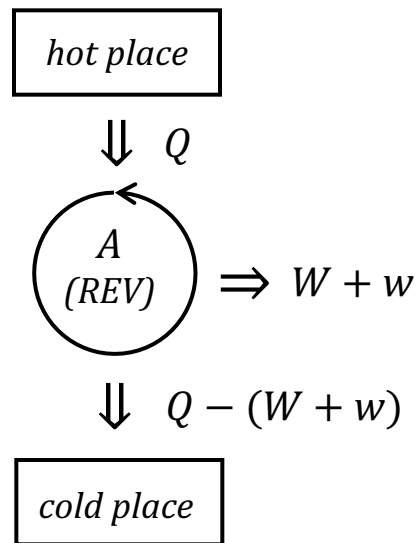
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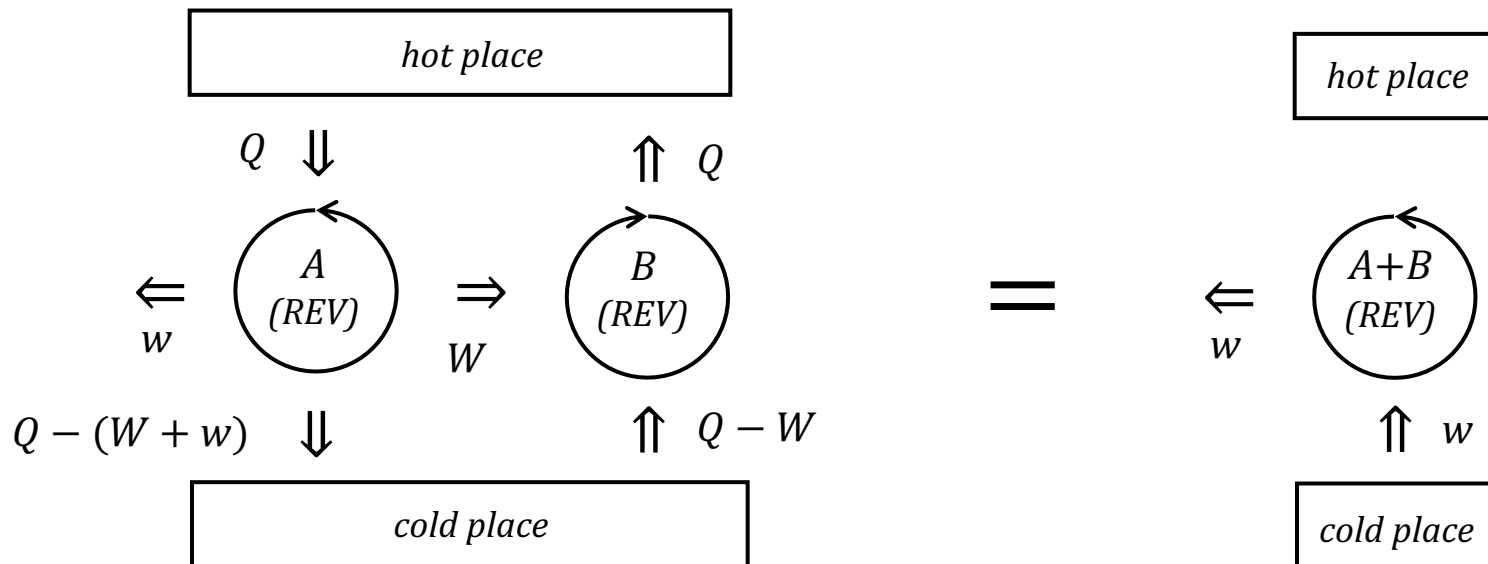
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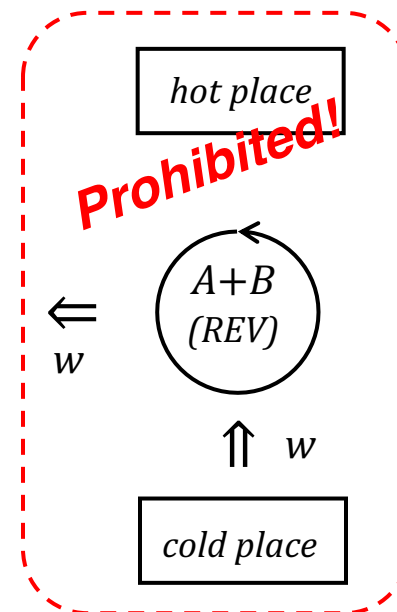
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Thomson: This is impossible!



"It is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects."



Claim 2. The efficiency of any heat engine, reversible or irreversible, only depends on the *temperature* of the hot and cold places; *not* on the working fluid.

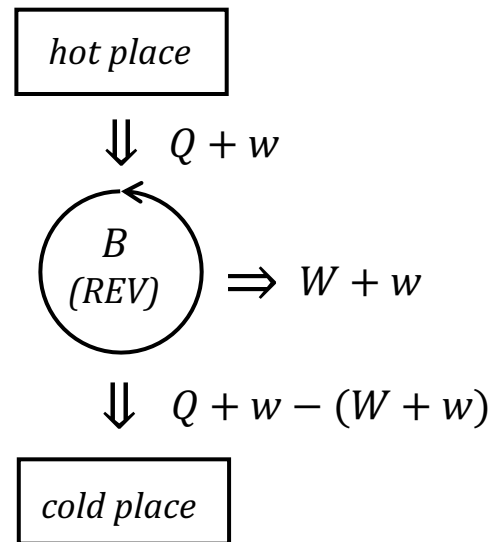
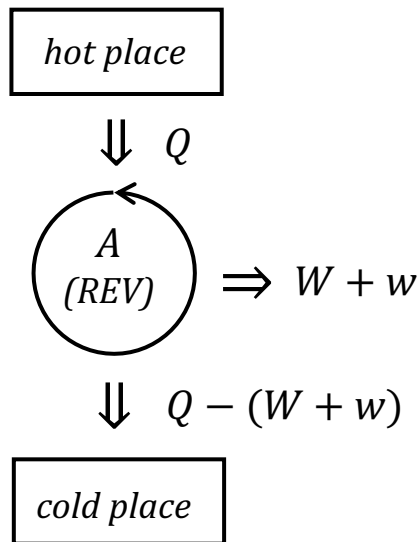
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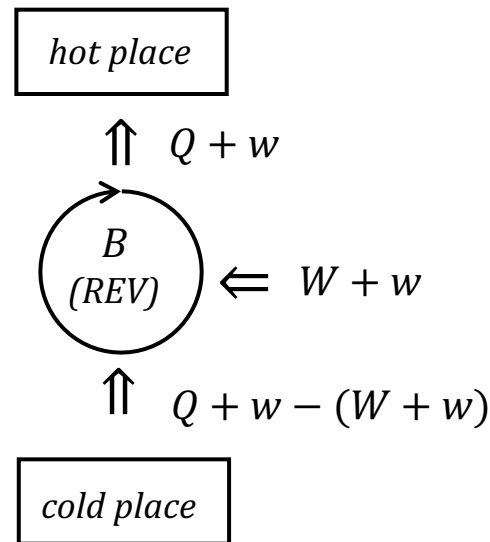
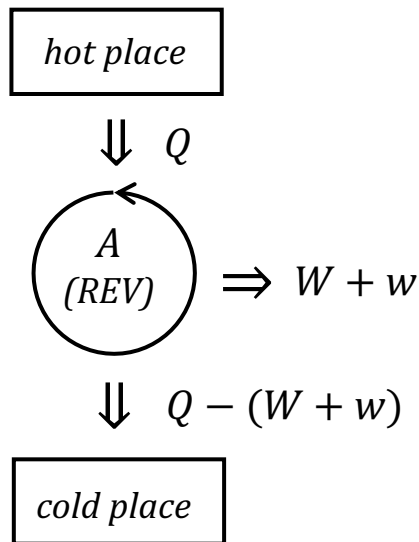
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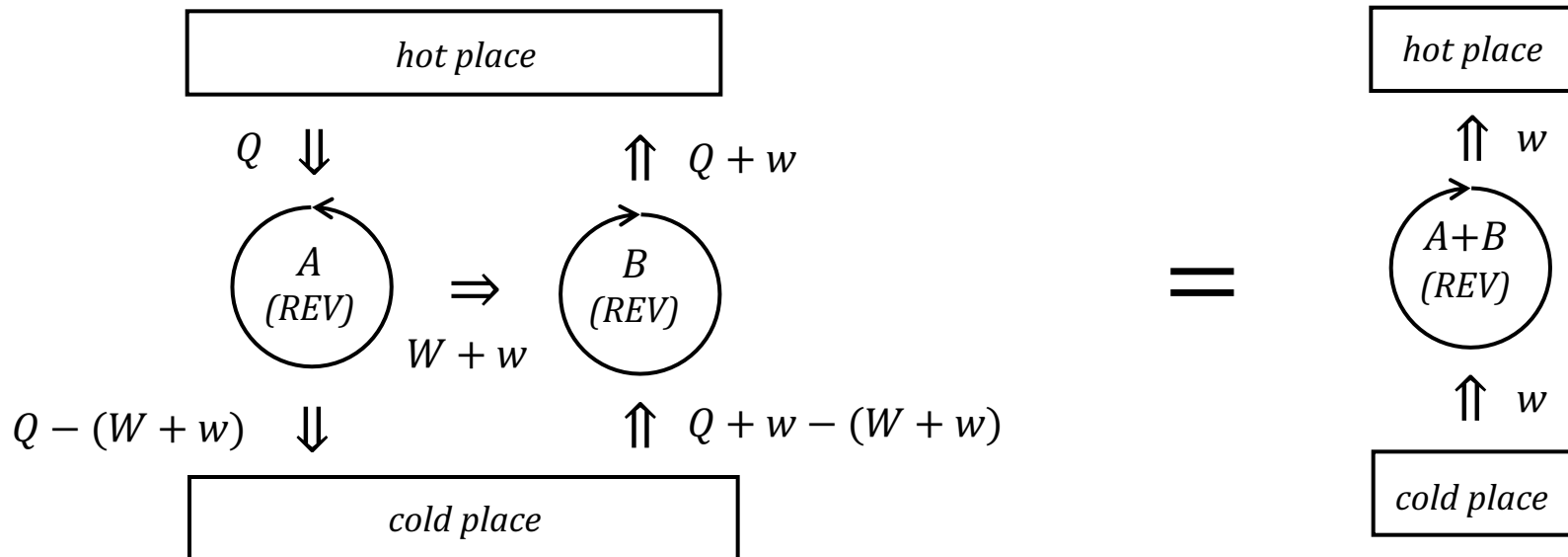
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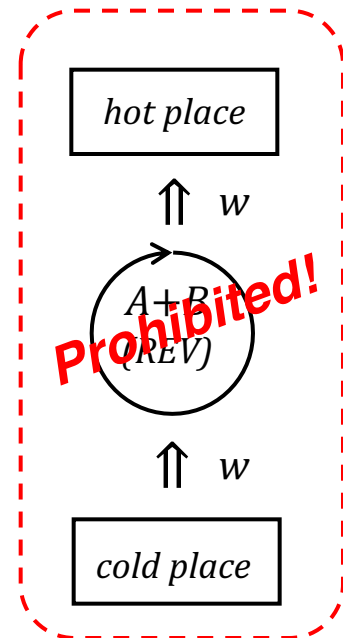
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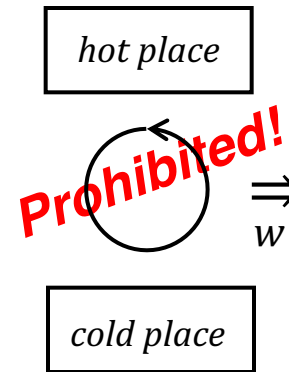


"[Heat] everywhere exhibits the tendency to annul differences of temperature, and therefore to pass from a warmer body to a colder one."

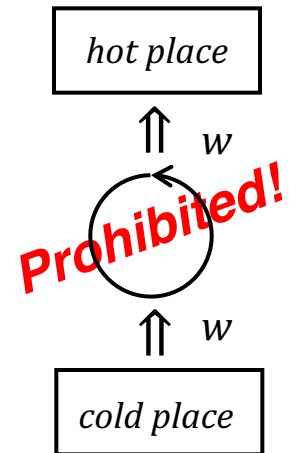


Three types of prohibited heat engines

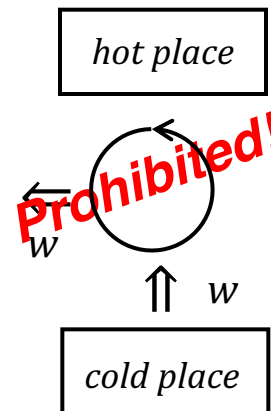
- (a) Carnot: Cyclic process in which work is produced without fall of heat (perpetual motion machine).



- (b) Clausius: Cyclic process in which heat is transferred from cold to hot place with no work input.



- (c) Thomson: Cyclic process in which there is a conversion of heat to work with no exhaust.



Prohibitions on (b) and (c) are known as the Clausius and Kelvin forms of the 2nd Law, respectively.

3. Second Law: Thermodynamic Entropy Version

Clausius' Inequality

- Clausius' "Fundamental Principle" (1854):



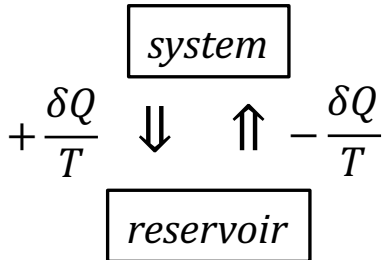
"Heat can never pass from a colder to a warmer body *without some other change, connected therewith, occurring at the same time.*"

Now formulate this "algebraically"...

- Consider a cyclic process involving infinitesimal transfers of heat $\delta Q/T$ between a system and a reservoir at lower temperature T :



"The algebraic sum of all the transformations which occur in a cyclical process can only be positive." (1854)



Or: $\oint \frac{\delta Q}{T} \geq 0$

Why? If sum were negative, then overall effect would be a passage of heat from lower to higher temp.
Moreover: If the process is reversible, then the sum must be zero.
 - It can't be negative.
 - If it were positive, the process could be reversed to produce a negative result.

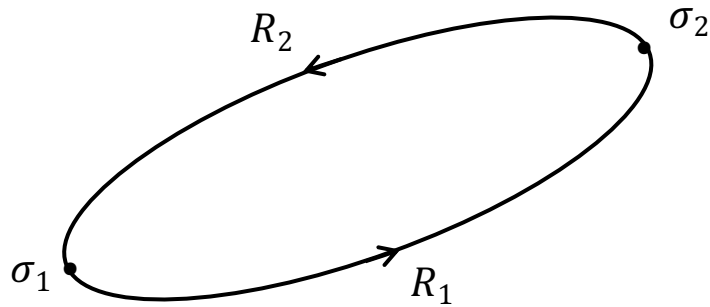
- 1865: Change of sign convention:
 - Let $+\delta Q/T$ represent absorption of heat by the system.
 - Let $-\delta Q/T$ represent emission of heat by the system.

$$\oint \frac{\delta Q}{T} \leq 0$$

Clausius' Inequality
In a cyclic process involving exchanges of heat between a system and a reservoir at lower temperature, the total amount of heat absorbed by the system is either zero (for a reversible process) or negative (for an irreversible process).

Thermodynamic Entropy S_{TD}

- Consider a system interacting with a reservoir via a *reversible* cycle:



Reversible cycle consisting of

- a reversible process R_1 from equilibrium state σ_1 to equilibrium state σ_2 ,*
- A reversible process R_2 from σ_2 back to σ_1 .*

- Clausius' inequality is $\oint \frac{\delta Q_R}{T} = \int_{R_1}^{\sigma_2} \frac{\delta Q_R}{T} + \int_{R_2}^{\sigma_1} \frac{\delta Q_R}{T} = 0$

- Thus: $\int_{R_1}^{\sigma_2} \frac{\delta Q_R}{T} = - \int_{R_2}^{\sigma_1} \frac{\delta Q_R}{T} = \int_{R_2}^{\sigma_2} \frac{\delta Q_R}{T}$

- So: $\int_{\sigma_1}^{\sigma_2} \frac{\delta Q_R}{T}$ is *path-independent*!

- Which means: It can be represented by a path-independent function S_{TD} :

$$\Delta S_{\text{TD}} = S_{\text{TD}}(\sigma_2) - S_{\text{TD}}(\sigma_1) \equiv \int_{\sigma_1}^{\sigma_2} \frac{\delta Q_R}{T}$$

*"thermodynamic
entropy"*

"... I propose to call the magnitude $[S_{\text{TD}}]$ the [thermodynamic] *entropy* of the body... I have intentionally formed the word *entropy* so as to be as similar as possible to the word *energy*; for the two magnitudes to be denoted by these words are so nearly allied in their physical meanings, that a certain similarity in designation appears to be desirable." (1865)



Def. 1 (*Thermodynamic entropy*). The **thermodynamic entropy** $S_{\text{TD}}(\sigma_2)$ of an equilibrium state σ_2 is the ratio of the change in heat to temperature of a *reversible* process that connects an initial equilibrium state σ_1 to σ_2 :

$$S_{\text{TD}}(\sigma_2) \equiv \int_{\sigma_1}^{\sigma_2} \frac{\delta Q_R}{T} + S_0 \quad \leftarrow \text{arbitrary constant}$$

Characteristics

1. Only defined for a system undergoing a *reversible process*.
2. Only defined for a system in *equilibrium states*.
3. For infinitesimal changes in S_{TD} , can write

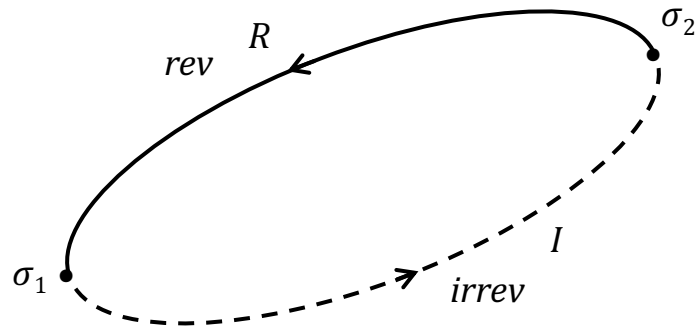
$$dS_{\text{TD}} = \delta Q_R / T$$

1/T is an 'integrating factor' that converts a path-dependent function Q into a path-independent function S_{TD}

- No reference to "disorder" or "chaos"!
- No reference to molecules or particles (gas or otherwise)!
- No reference to "information"!

Principle of Non-Decreasing S_{TD}

Consider a system interacting with a reservoir via an *irreversible* cycle:



Irreversible cycle consisting of

- *an irreversible process I from equilibrium state σ_1 to equilibrium state σ_2 ,*
- *a reversible process R from σ_2 back to σ_1 .*

- Clausius' inequality is
$$\int_I^{\sigma_2} \frac{\delta Q}{T} + \int_R^{\sigma_1} \frac{\delta Q_R}{T} < 0 \quad \text{or} \quad \int_I^{\sigma_2} \frac{\delta Q}{T} - \int_R^{\sigma_1} \frac{\delta Q_R}{T} < 0$$

- Thus:
$$\Delta S_{\text{TD}} = \int_R^{\sigma_2} \frac{\delta Q_R}{T} > \int_I^{\sigma_2} \frac{\delta Q}{T}$$
 ← Recall: If the cycle was reversible (i.e., if process I was reversible), then > would become =.

- So in general:
$$\Delta S_{\text{TD}} = \int_R^{\sigma_2} \frac{\delta Q_R}{T} \geq \int_{\sigma_1}^{\sigma_2} \frac{\delta Q}{T}$$

- Now: Suppose the irreversible process is *thermally isolated*; i.e., $\delta Q = 0$.

- Then:

$\Delta S_{\text{TD}} \geq 0 \quad \text{or} \quad S_{\text{TD}}(\sigma_2) \geq S_{\text{TD}}(\sigma_1)$

The change in thermodynamic entropy for a thermally isolated irreversible process between equilibrium states increases, and is unaltered for a reversible process.



"... [W]e may express in the following manner the fundamental laws of the universe which correspond to the two fundamental theorems of the mechanical theory of heat:

1. *The energy of the universe is constant.*
2. *The [thermodynamic] entropy of the universe tends to a maximum."* (1865)

Aside: S_{TD} and the Approach to Equilibrium

- How does the Principle of Non-Decreasing S_{TD} relate to the Equilibrium Principle?



One way of formulating the 2nd Law!

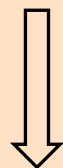
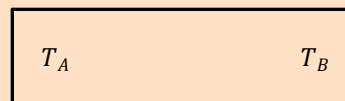
- The "approach to equilibrium" is a process that connects a *non-equilibrium* state with an equilibrium state!

How is S_{TD} defined for such a process? And does it increase/remains unaltered?

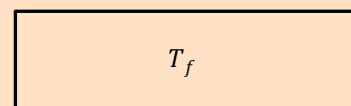
General method:

- System in initial *non-equilibrium* state can be decomposed into subsystems, each in an initial *equilibrium* state.
- Process that takes system from initial non-equilibrium state to final equilibrium state can be decomposed into a sum of processes that take each subsystem from its initial equilibrium state to final equilibrium state.
- Each sub-process has well-defined change in S_{TD} , and sum of these (i.e., change in S_{TD} for entire system) cannot be negative!

$T_A > T_B$
initial non-equilibrium state

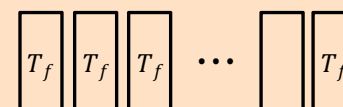
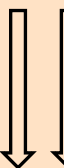
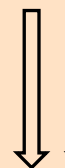
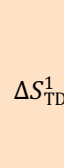
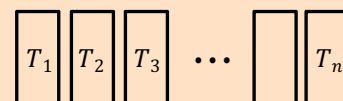


$$\Delta S_{TD} = \Delta S_{TD}^1 + \dots + \Delta S_{TD}^n$$



final equilibrium state

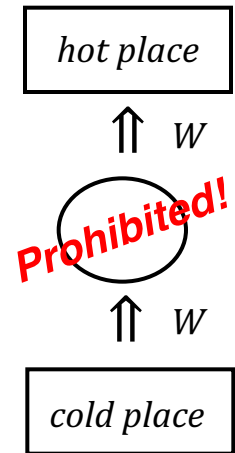
$T_1 = T_A < T_2 < \dots < T_n = T_B$
initial equilibrium states



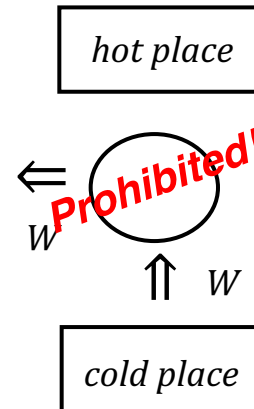
final equilibrium states

Summary of 2nd Law of Thermodynamics

(1) Clausius Form: No cyclic process in which heat is transferred from cold to hot place without work input:



(2) Thomson Form: No cyclic process in which there is a conversion of heat to work without exhaust:



Consequence of 2nd Law:

The *thermodynamic entropy* S_{TD} of a thermally isolated irreversible process between equilibrium states increases, and is unaltered for a reversible process.

Absolute statements!

Meant to hold for any system subject to thermodynamical analysis.

Summary of Entailments

2nd Law
(Clausius Version)

There can be no cyclic process whose sole effect is the transfer of heat from a cold place to a hot place.



2nd Law
(Thomson Version)

There can be no cyclic process whose sole effect is the extraction of heat from a source and the performance of an equivalent amount of heat.



Clausius'
Inequality

In a cyclic process, the sum of all transformations $\delta Q/T$, consisting of an element of heat δQ absorbed by the system at temperature T , must be less than or equal to zero:

$$\oint \frac{\delta Q}{T} \leq 0$$


2nd Law
(Entropy Version)

The thermodynamic entropy of a thermally isolated system increases in any irreversible process and is unaltered in a reversible process:

$$\Delta S_{TD} \geq 0$$