"Nobody really knows what entropy really is"

John von Neumann
(1903-1957)

How so?

The **thermodynamic entropy** $S_{\mathrm{TD}}(\sigma_2)$ of a state σ_2 of a physical system is the ratio of the change in heat δQ_R to temperature T of a reversible process that connects an initial state σ_1 to σ_2:

$$S_{\mathrm{TD}}(\sigma_2) \equiv \int_{\sigma_1}^{\sigma_2} \frac{\delta Q_R}{T} + \text{const.}$$

Thermodynamics! (1860s)
- *energy*
- *heat*
- *work*
- *2nd Law!*

The **von Neumann entropy** $S_{\mathrm{vN}}(\rho)$ of a density operator state ρ is given by:

$$S_{\mathrm{vN}}(\rho) \equiv -\mathrm{Tr}\,(\rho \ln \rho)$$

Quantum Mechanics! (1920s-30s)
- *entanglement!*

The **entanglement entropy** S_A of a subsystem A of a bipartite system AB is defined as the von Neumann entropy of ρ_A:

$$S_A \equiv S(\rho_A) = -\mathrm{Tr}\,(\rho_A \ln \rho_A)$$

The **Boltzmann entropy** $S_{\mathrm{Boltz}}(\Gamma_M)$ of a macrostate Γ_M of size $|\Gamma_M|$ is given by:

$$S_{\mathrm{Boltz}}(\Gamma_M) \equiv \ln|\Gamma_M|$$

Statistical Mechanics! (1870s-80s)
- *multi-particle systems*
- *probabilities!*

The **Gibbs entropy** $S_{\mathrm{Gibbs}}(\rho)$ of a distribution ρ is the ensemble average of the quantity $-\ln\rho$:

$$S_{\mathrm{Gibbs}}(\rho) \equiv -\,k \int_{\Gamma} \rho(x) \ln\rho(x)\,dx$$

General Relativity! (1930s-70s)
- *black holes*
- *information loss paradox!*

The **Bekenstein-Hawking entropy** of a black hole is given by

$$S_{\mathrm{BH}} \equiv \mathrm{Area(horizon)}/4$$

The **Shannon entropy** $S_{\mathrm{Shan}}(X)$ of a random variable X with possible values $\{x_1, \ldots, x_\ell\}$ and probability distribution $\{p_1, \ldots, p_\ell\}$ is given by:

$$S_{\mathrm{Shan}}(X) = -\sum_i p_i \log_2 p_i$$

Classical Information Theory! (1940s)
- *"information"!*
- *uncertainty*

How are all of these quantities related (if at all)?

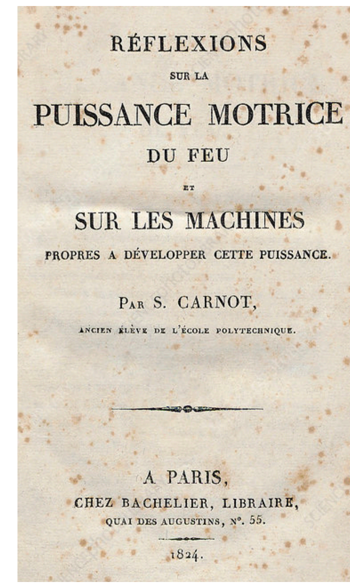
- *How does a concept introduced in one particular field of physics evolve over time to affect other, seemingly unrelated, fields?*

01. Heat Engines and the Second Law

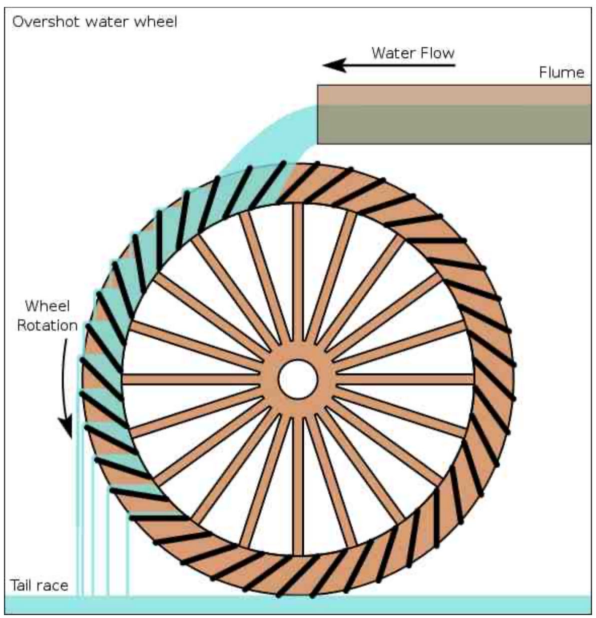
1. Carnot and Heat Engines

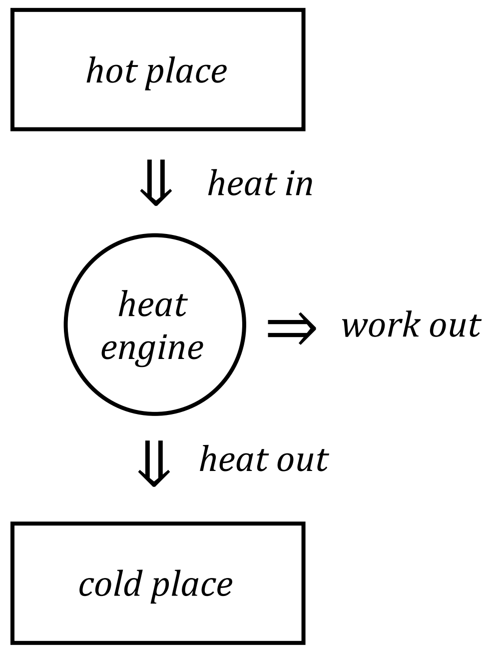
- Carnot, S. (1824) "Reflections on the Motive Power of Fire".
- *Idea*: Treat heat in analogy with water as a substance that produces mechanical effect (work) when it "falls" from a hot place to a cold place.

Sadi Carnot
(1796-1832)

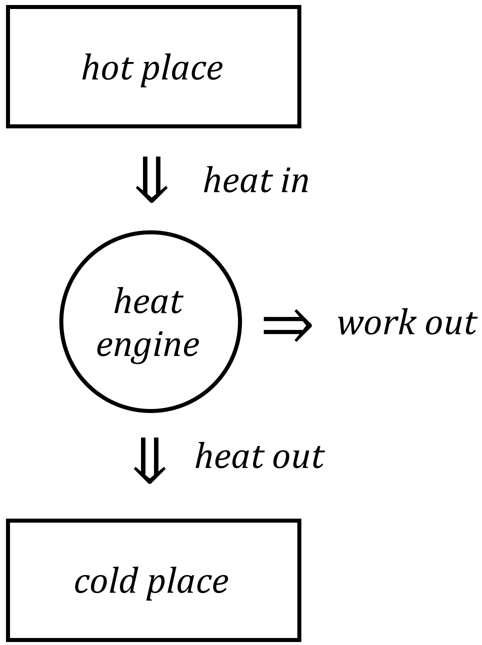

RÉFLEXIONS
SUR LA
PUISSANCE MOTRICE
DU FEU
ET
SUR LES MACHINES
PROPRES A DÉVELOPPER CETTE PUISSANCE.
PAR S. CARNOT,
ANCIEN ÉLÈVE DE L'ÉCOLE POLYTECHNIQUE.

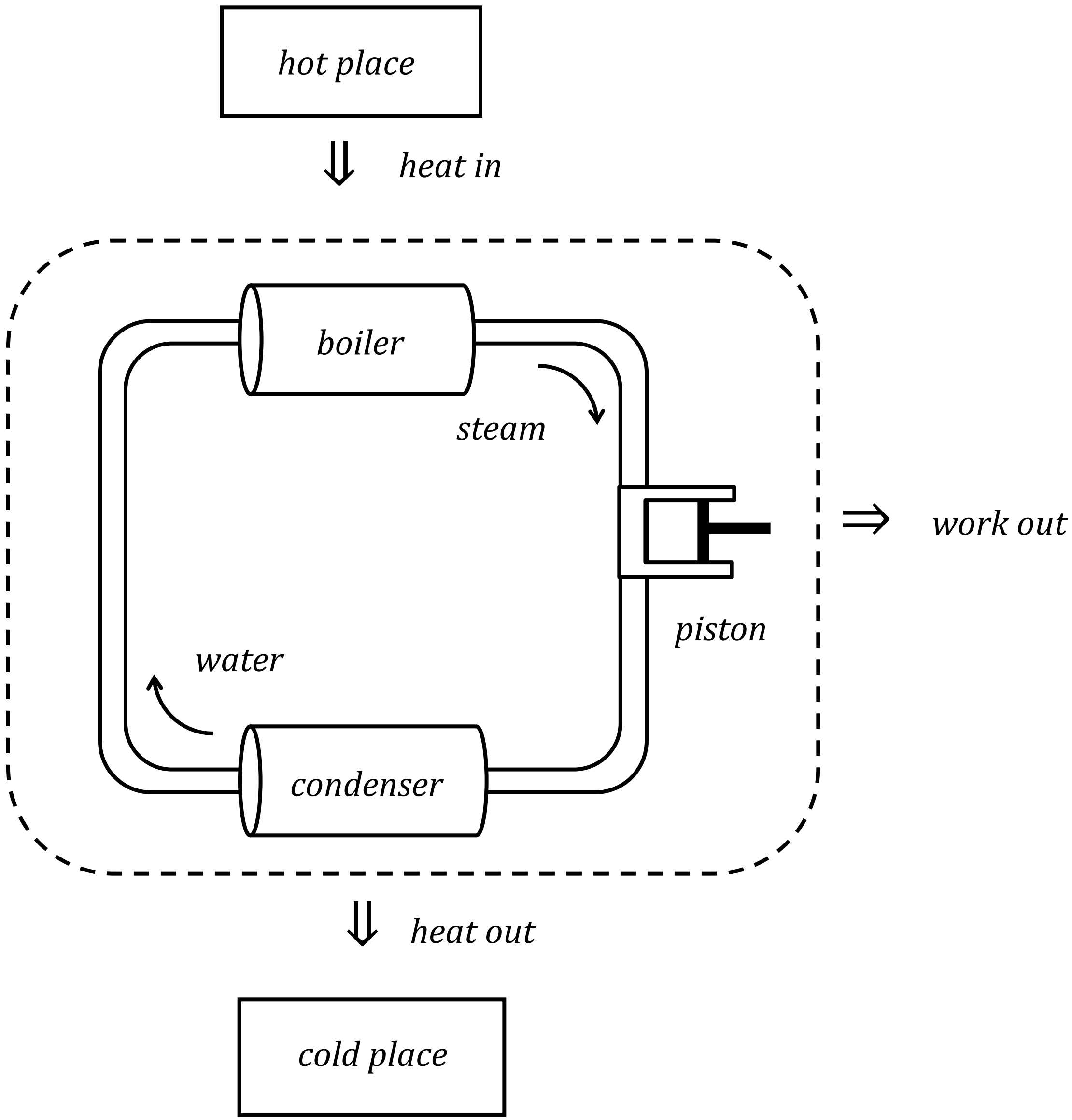
A PARIS,
CHEZ BACHELIER, LIBRAIRE,
QUAI DES AUGUSTINS, N°. 55.
1824.





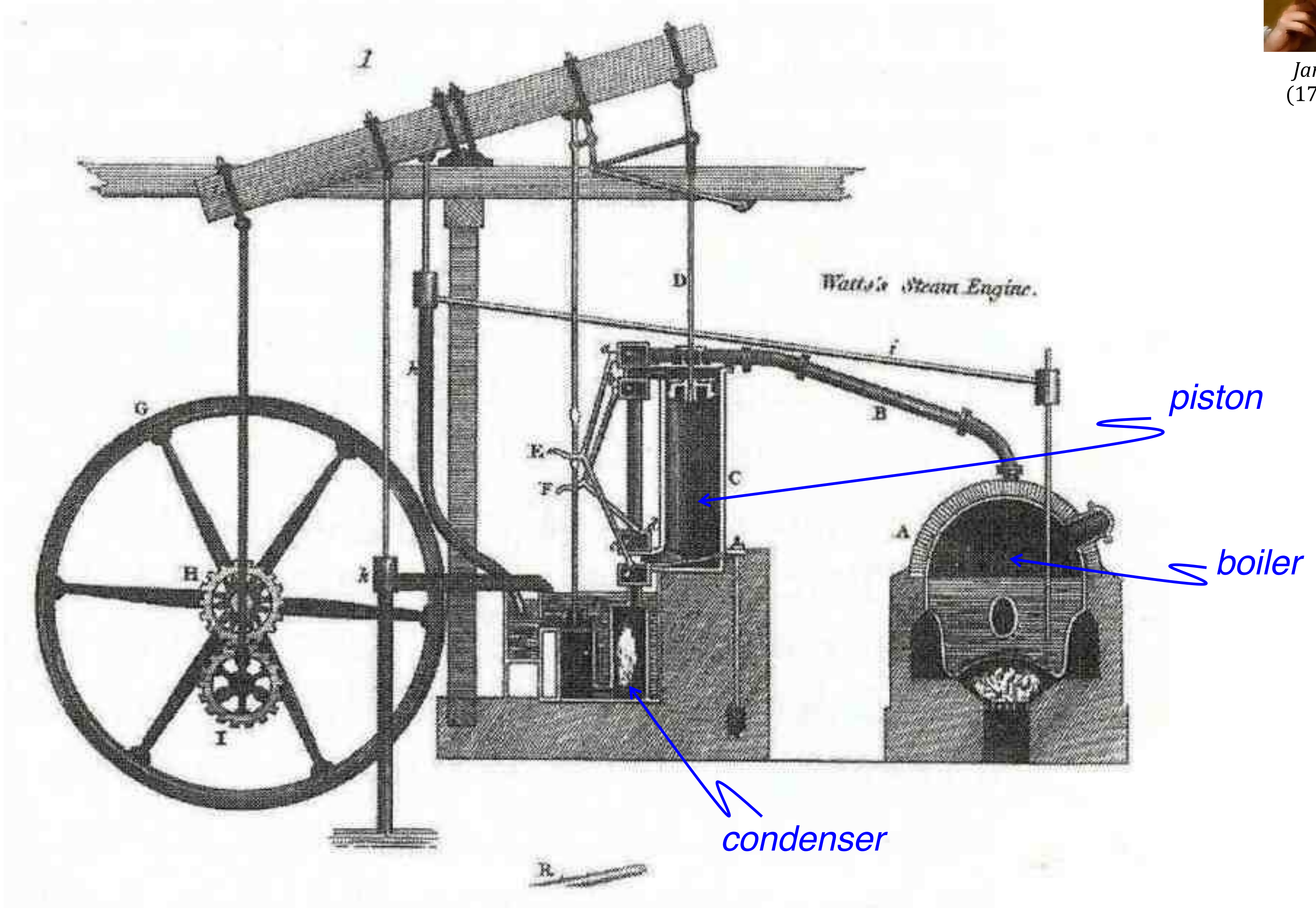
- Heat engine of economic interest: Steam engine!





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

James Watt
(1736-1819)

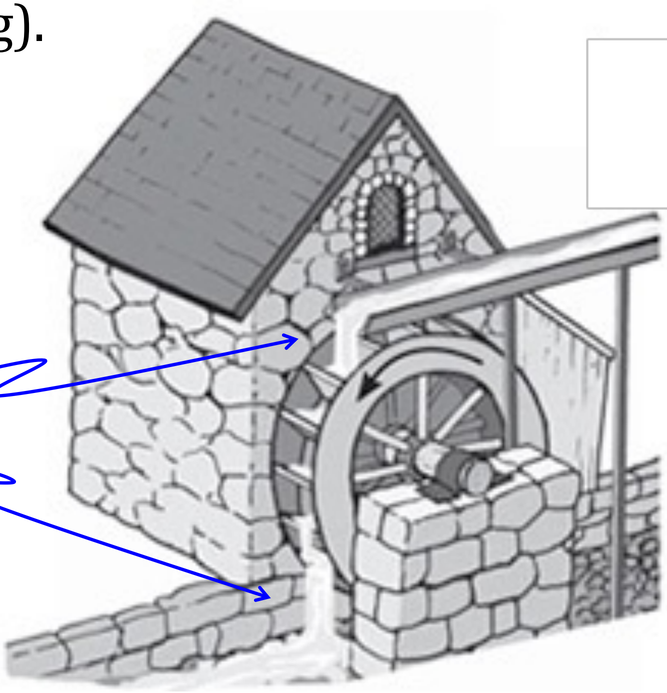


- *<u>Important question</u>*: What is the *maximally efficient* heat engine (*i.e.*, maximizes work output while minimizing waste)?

Maximum efficiency is obtained when heat-flow between hot place and engine, and engine and cold place, occurs at *equal temperatures*.

- *<u>Analogy with water-wheel:</u>* Maximum efficiency obtained when water-flow between stream and water-wheel occurs at *equal heights* (minimizes splashing).

minimize splashing at
high flume and low flume



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

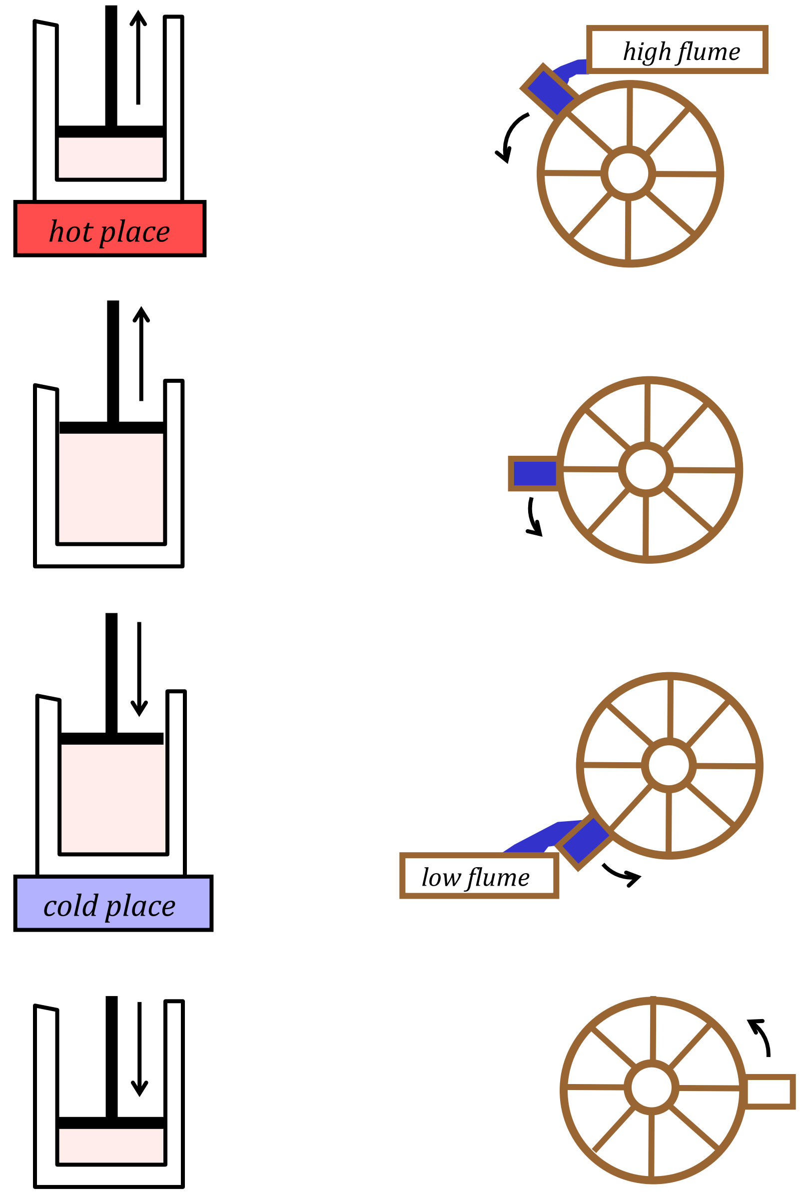
Analogy: *temperature ≈ height, heat ≈ water*

1-2: *Isothermal expansion*
- Heat absorbed at constant temp.
- Gas expands, doing work.
- Pressure decreases, volume increases.

2-3: *Adiabatic expansion*
- Temp decreases at constant heat.
- Gas expands, doing work.
- Pressure decreases, volume increases.

3-4: *Isothermal contraction*
- Heat exhausted at constant temp.
- Gas contracts.
- Pressure increases, volume decreases.

4-1: *Adiabatic contraction*
- Temp increases at constant heat.
- Gas contracts.
- Pressure increases, volume decreases.



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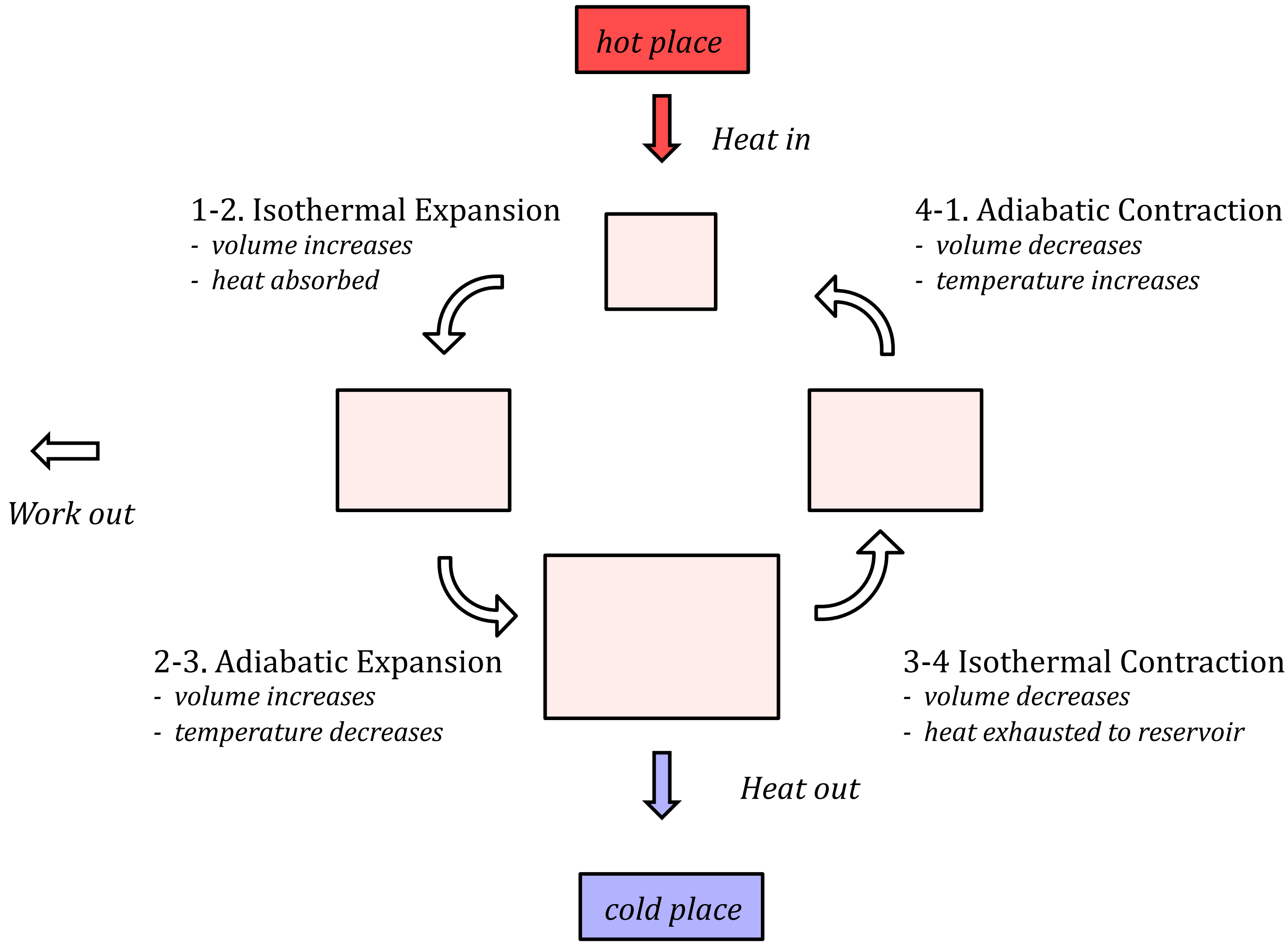


Carnot's Two Claims:

(1) Maximally efficient heat engines are *reversible*. Real engines can only aspire to be reversible.

(2) Efficiency (work done per heat input) of any heat engine (reversible or irreversible) only depends on the *temperature* of the hot and cold places; *not* on the working fluid.

Big Question: What is the nature of heat?

- *Carnot*: Caloric theory of heat.
  - *Heat ("caloric") is a substance that "falls" from hot places to cold places and in the process generates work.*

Like water, no heat is lost during this process.

- *But*: Suppose heat can be converted into work (unlike water!).

Then a portion of the "falling" heat gets converted into work and the remainder, less than the initial amount, ends up in the cold place.

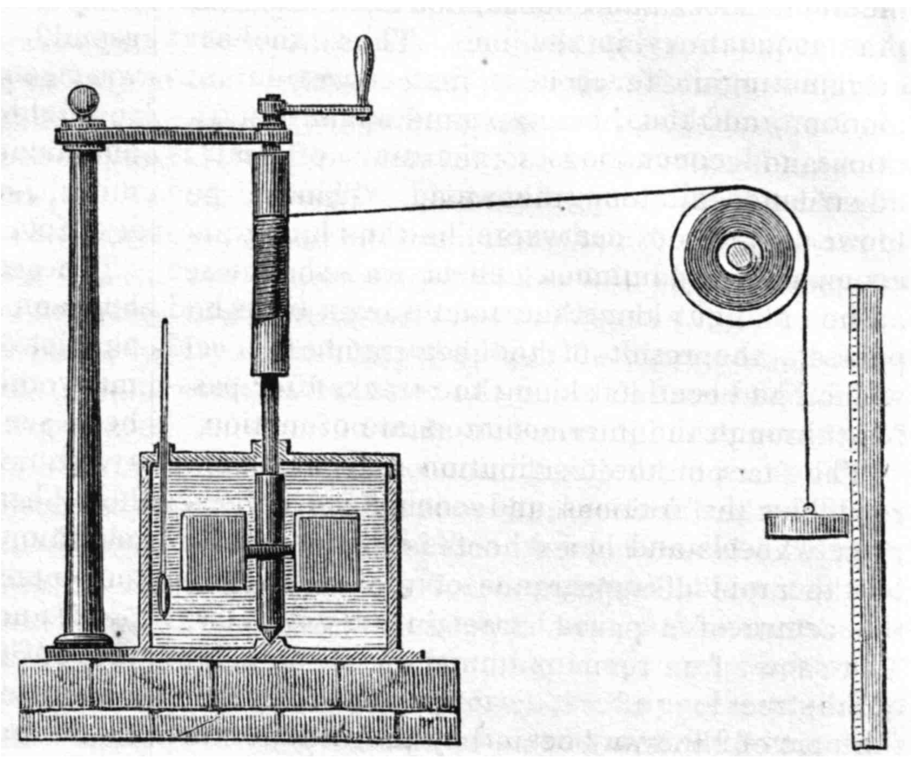
- *Moreover*: Suppose heat isn't a substance like water.

Suppose it's something different...

"[If] we consider heat not as a substance, but as *a state of vibration*, there appears to be no reason why it should not be induced by an action of a simply mechanical character." (1843)

James Prescott Joule
(1818-1889)

- Paddle wheel experiment (1845): Thermally isolated paddle wheel rotating in container of water (doing work) generates heat!



Claim. Heat and work are interconvertible: Work can be converted into heat *and* heat can be converted into work.

Two Key Empirical Results:

(a) Mechanical equivalent of heat:

"When the temperature of a pound of water is increased by one degree of Fahrenheit's scale, an amount of *vis viva* is communicated to it equal to that acquired by a weight of 890 pounds after falling from the altitude of one foot." (1845.)

(b) The amount of work required to take the isolated water system between the same two equilibrium states is independent of the method used to generate it.

- *Different weights, different drop heights.*
- *Use electric current instead of weights.*

These results eventually become the "First Law of Thermodynamics"...

First Law of Thermodynamics

- *Thermally isolated system*:
  The "adiabatic" ("constant heat") work $W_{\text{adiabatic}}$ necessary to take a thermally-isolated system from one equilibrium state to another is *independent of the process used*.

This means it can be represented by a path-independent function, call it "internal energy" U

$$W_{\text{adiabatic}} = \underbrace{U(\sigma_2)}_{\text{"internal energy" of final state } \sigma_2} - \underbrace{U(\sigma_1)}_{\text{"internal energy" of initial state } \sigma_1} = \Delta U$$

- For infinitesimal changes in $W_{\text{adiabatic}}$, can write:

$$dW_{\text{adiabatic}} = dU$$

> dU is an *exact differential*: Its integral $\int_{\sigma_1}^{\sigma_2} dU$ between two states only depends on the values of U at those states.

First Law of Thermodynamics

- *For a non-thermally isolated system*:
  The change in internal energy of a non-thermally isolated system from one equilibrium state to another is equal to the work done on the system by its environment and the *heat* absorbed by it from its environment:

$$\Delta U = \underbrace{W}_{\text{positive for work done on system}} + \underbrace{Q}_{\text{positive for heat absorbed by system}}$$

Def. (*Heat*). **Heat $\boldsymbol{Q}$** is the non-mechanical exchange of energy between a thermodynamic system and its environment due to their temperature difference.

- *For a non-thermally isolated system, there may be temp-dependent interactions between system and environment so that the work needed to take the system between equilibrium states may depend on the process used.*
- *Different processes may involve different types of interactions with the environment.*
- *This means (non-adiabatic) work W and heat Q are "path-dependent" functions.*

- For infinitesimal changes in U, can write:

$$dU = \delta W + \delta Q$$

δW and δQ are *inexact differentials*: Their integrals $\int_{\sigma_1}^{\sigma_2} \delta W$, $\int_{\sigma_1}^{\sigma_2} \delta Q$ between two states depend on the paths between the states.

2. Formulations of the Second Law

(i) Thomson's (1849) "An Account of Carnot's Theory"

- *Carnot's "Fundamental Principle"*: No heat lost in operation of a heat engine.

- *Concept of a "perfect thermo-dynamic engine"*:

> "A perfect thermo-dynamic engine is such that, whatever amount of mechanical effect it can derive from a certain thermal agency; if an equal amount be spent in working it backwards, an equal reverse thermal effect will be produced."

William Thomson
(later Lord Kelvin)
(1824-1907)

- Call this a *reversible* heat engine.

hot place

$\Downarrow$ $Q = heat\ in$

REV $\Rightarrow$ $W = work\ out$

$\Downarrow$ $Q = heat\ out$

cold place

Reverse it!

hot place

$\Uparrow$ Q

REV $\Leftarrow$ $W = work\ in$

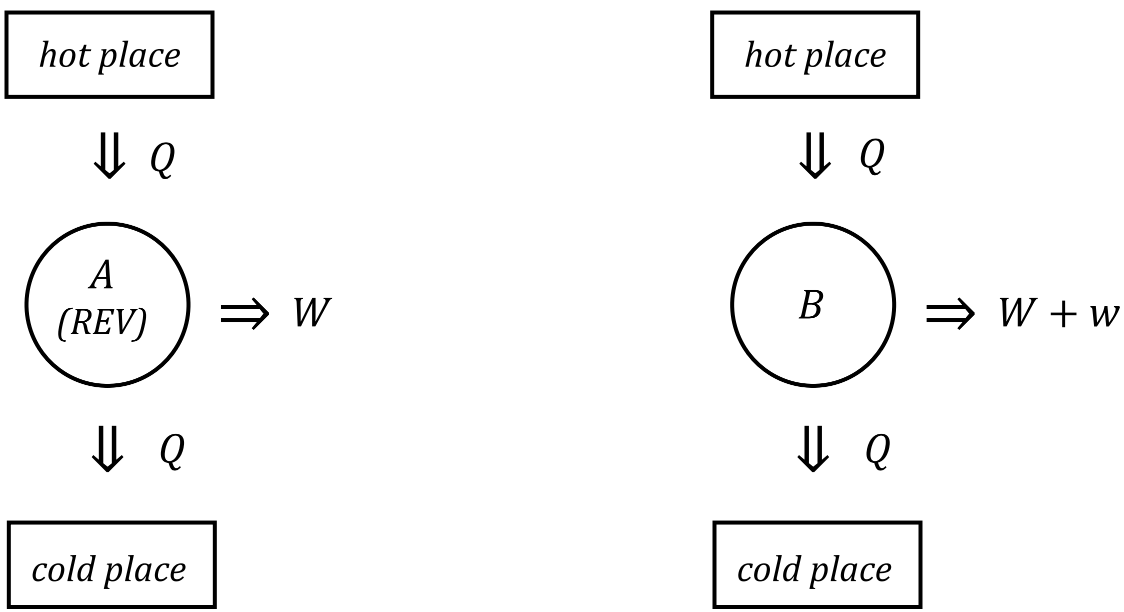
$\Uparrow$ Q

cold place

Carnot 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:

- 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.



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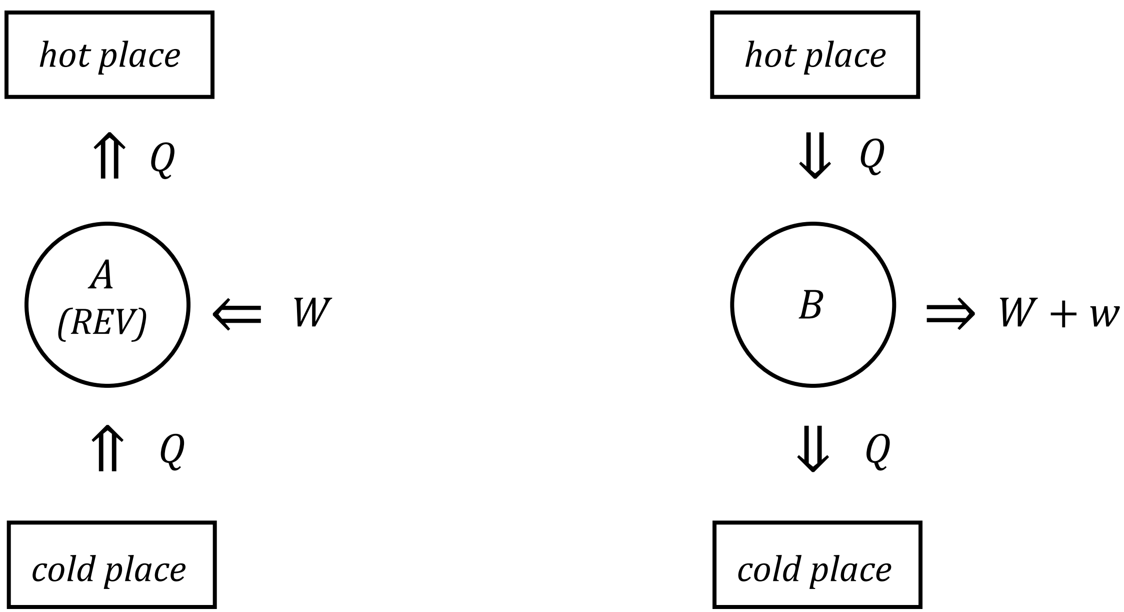

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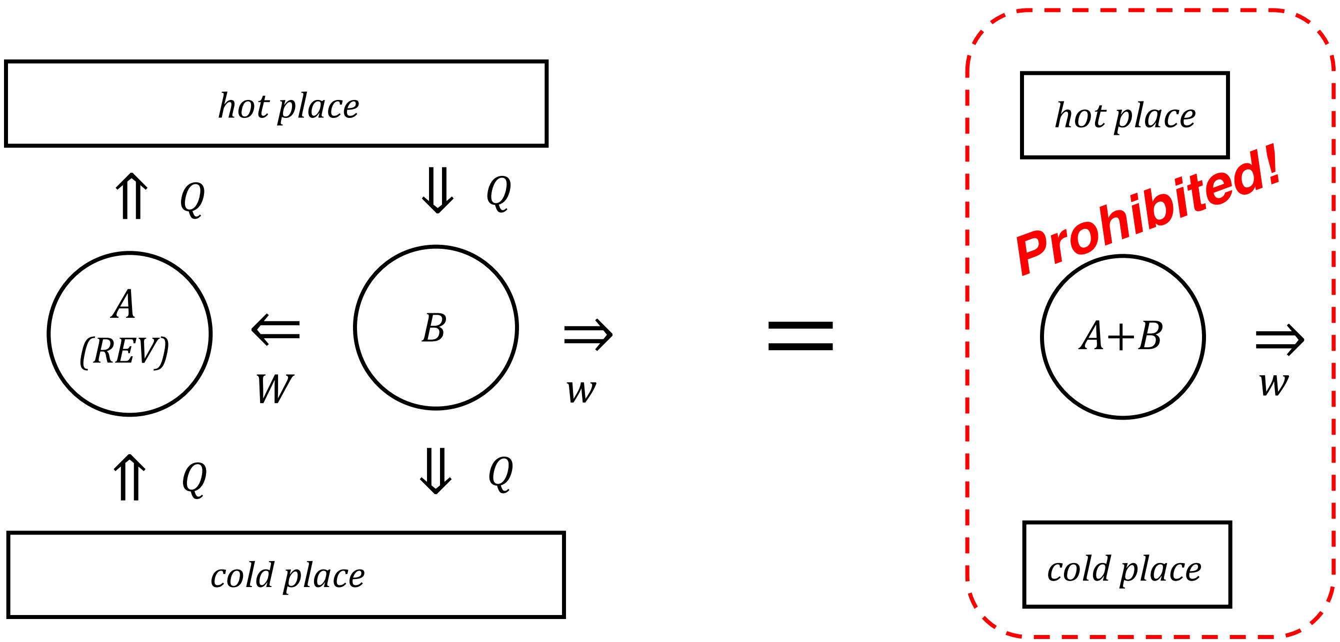
- Now reverse A and hook it up to B.
- Engine $A+B$ does work w for free (no net fall of heat required)!
  But, sez Carnot, this is impossible: a perpetual motion machine!



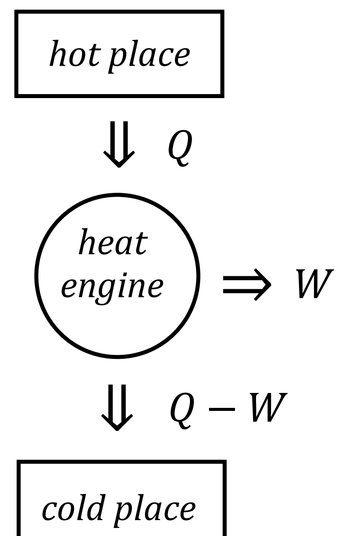
(ii) Clausius' (1850) "On the Moving Force of Heat".

- *1st Maxim (Joule's equivalence of work and heat)*:

> "In all cases where work is produced by heat, a quantity of heat proportional to the work done is expended; and inversely, by the expenditure of a like quantity of work, the same amount of heat may be produced."

Rudolph Clausius
(1822-1888)

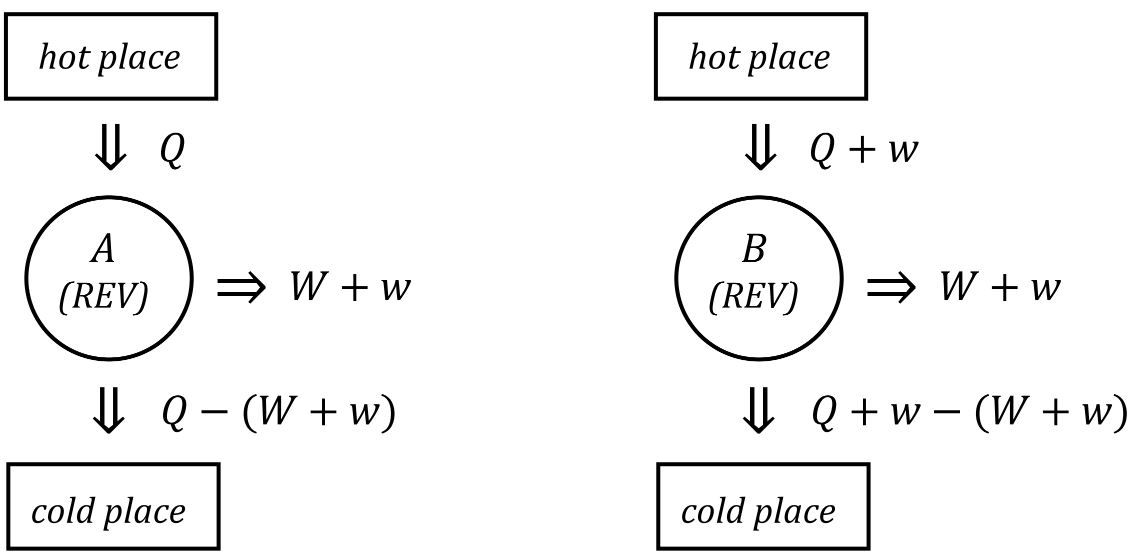
- *Carnot's Assumption*: In a heat engine, work is produced by the transmission of heat from a hot place to a cold place, *with no loss/gain of heat as a result*.
- *Clausius*: Accepts first clause (of Carnot's Assumption) as *2nd Maxim*, but rejects second clause (after Joule).
- *Consequences*:
  - Allows that the amount of heat associated with a process depends on the path taken and *not* on the initial and final states.
  - If Q_{in} is the heat falling from the hot place, and W is the work produced, then the heat expended to the cold place is $Q_{out} = Q_{in} - W$.



Carnot Claim #2: In an ideal (*i.e.*, reversible) heat engine, the work produced depends only on the quantity of heat transmitted (*i.e.*, the temperature of the hot and cold places), and not on the working fluid.

Clausius' Proof:

- Suppose A and B are reversible engines operating between the same hot and cold places, and A is more efficient (in the sense that B requires more heat to produce the same amount of work that A produces).
- Reverse B and hook it up to A.



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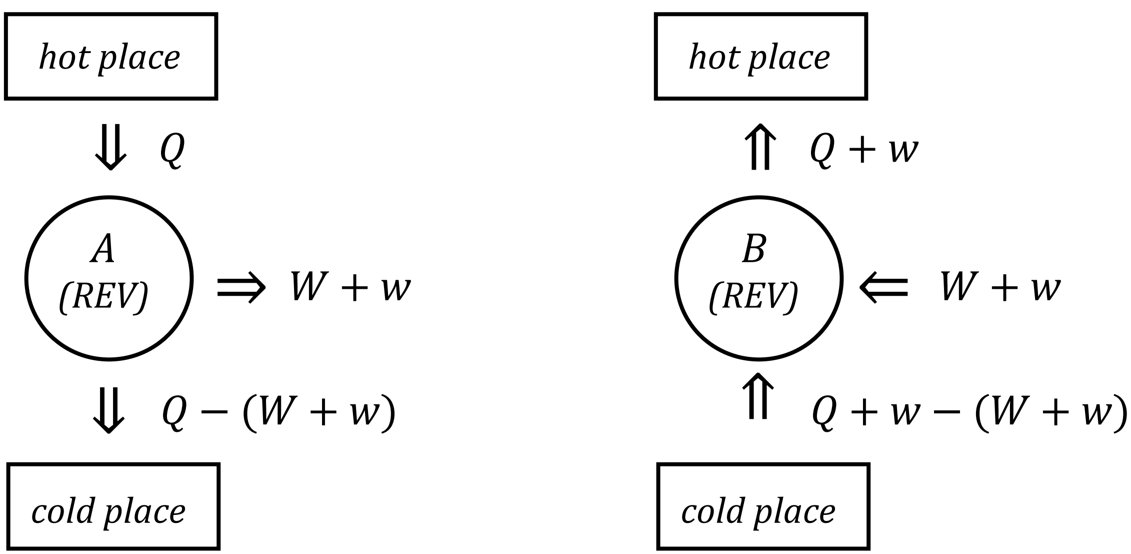

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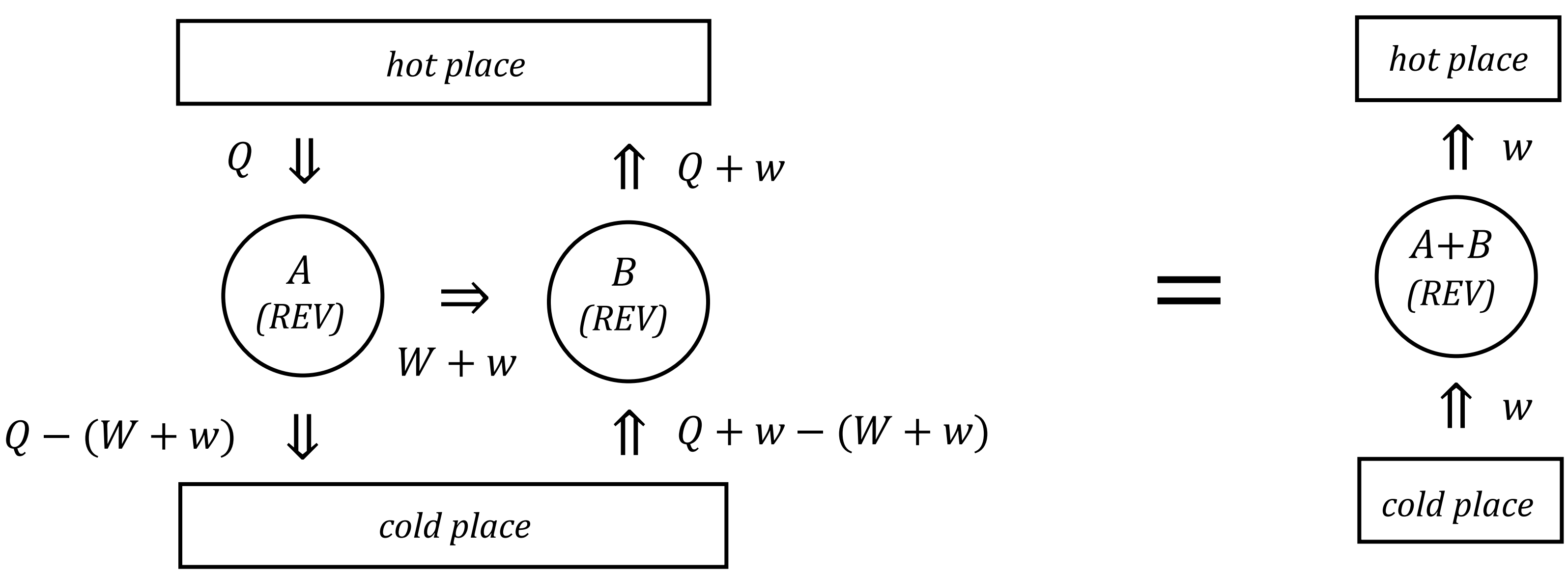
- Engine $A+B$ takes an amount of heat w from a cold place to a hot place with no work input!



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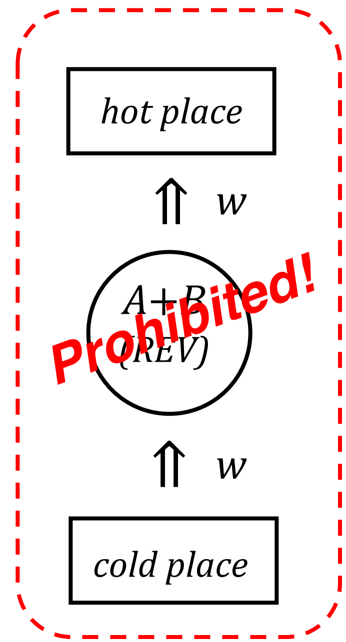
Clausius' Proof:

- Suppose *A* and *B* are reversible engines operating between the same hot and cold places, and *A* is more efficient (in the sense that *B* requires more heat to produce the same amount of work that *A* produces).
- Reverse *B* and hook it up to *A*.
- Engine *A*+*B* takes an amount of heat *w* from a cold place to a hot place with no work input!
- Clausius: This is impossible!

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



(iii) Thomson's (1851-55) "The Dynamical Theory of Heat"

- *Prop. 1 (Joule)*:

"When equal quantities of mechanical effect are produced by any means whatever from purely thermal sources, or lost in purely thermal effects, equal quantities of heat are put out of existence or are generated."

  - *Agrees with Joule but puzzled over what happens to work during conduction or friction.*

- *Prop. 2 (Carnot & Clausius)*:

"If an engine be such that, when it is worked backwards, the physical and mechanical agencies in every part of its motions are all reversed, it produces as much mechanical effect as can be produced by any thermodynamic engine, with the same temperature of source and refrigerator, from a given quantity of heat."

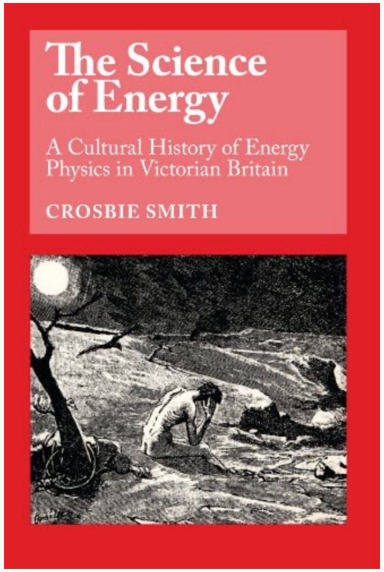
  - *In other words (Carnot Claim #1): The most efficient heat engine for any given hot and cold places is a reversible heat engine.*

Now seeks a theological foundation for Prop. 2...

- *Thomson on conduction and friction*:

"The fact is, it may I believe be demonstrated the work is lost to man irrecoverably; but not lost in the material world... Although no destruction of energy can take place in the material world without an act of power possessed only by the supreme ruler, yet transformations take place which remove irrecoverably from the control of man sources of power which, if the opportunity of turning them to his own account had been made use of, might have been rendered available."

- *Smith (1998)*: God has ordained for nature two basic laws of energy: its conservation and its progressive transformation.
- *Thomson*: "Everything in the physical world is progressive."
- *Smith's gloss*: Reflects a "Presbyterian economy of nature".
  - *Energy = gift from God*.
  - *Only God can restore* it.
  - *Humans can transform it and distribute it, but in doing so lose some of it*.



Smith, C. (1998)
The Science of Energy

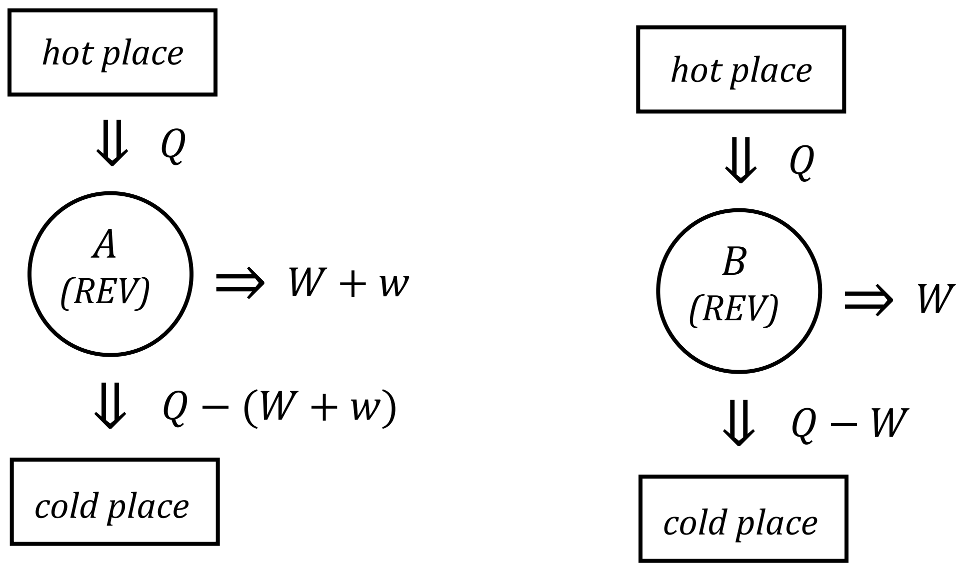
- *Thomson now claims*:

"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."

- *In other words*: No heat engine can produce as its sole effect the complete conversion of heat to work (there must be "exhaust" heat).

Thomson's Proof of Prop. 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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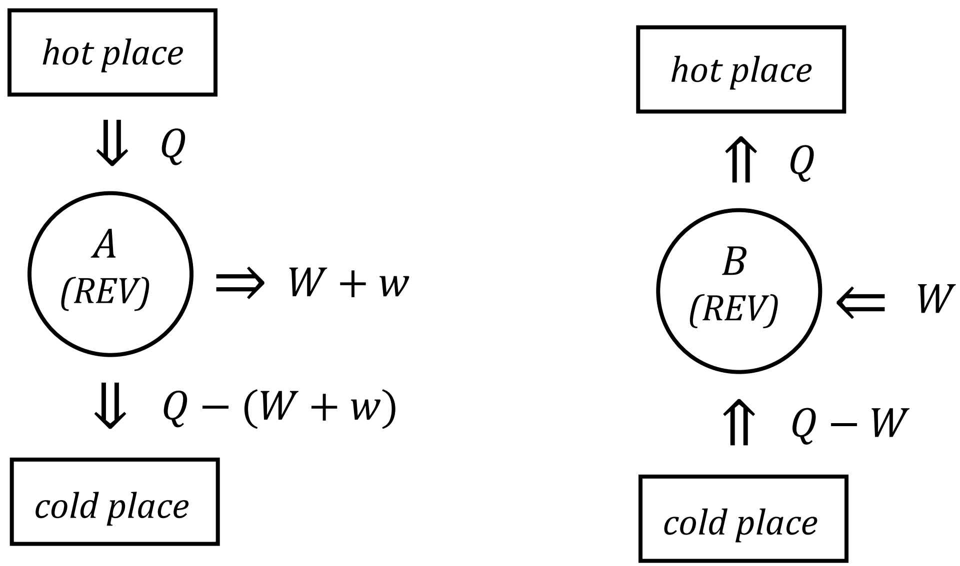
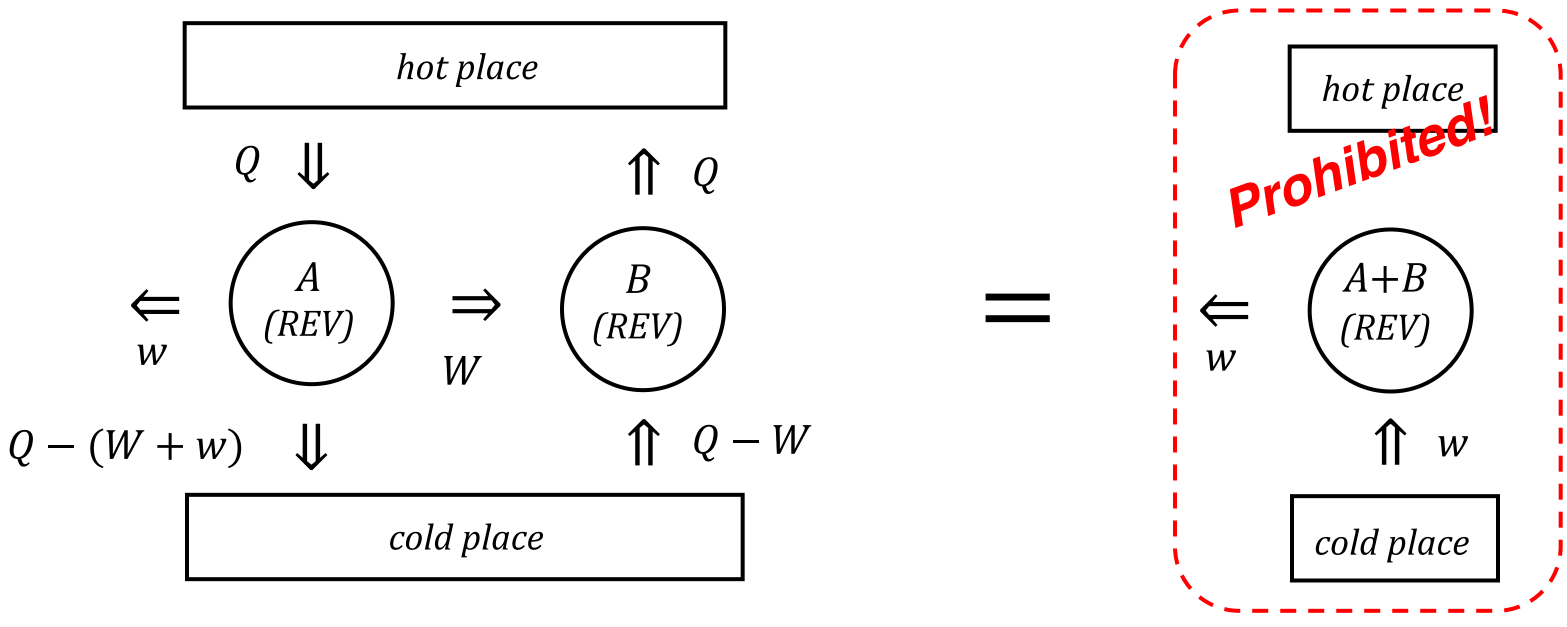


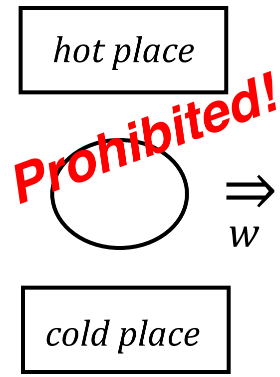
Thomson's Proof of Prop. 2

- 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.
- Engine $A+B$ converts heat to work with no exhaust.

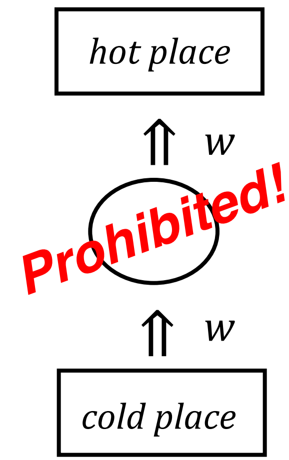


Three types of prohibited heat engines

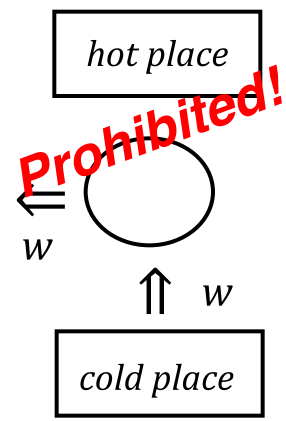
(a) *Carnot*: Work done without fall of heat (perpetual motion machine).



(b) *Clausius*: Heat transfer from cold to hot place with no work input.



(c) *Thomson*: Conversion of heat to work with no exhaust.



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