I. Carnot and Heat Engines
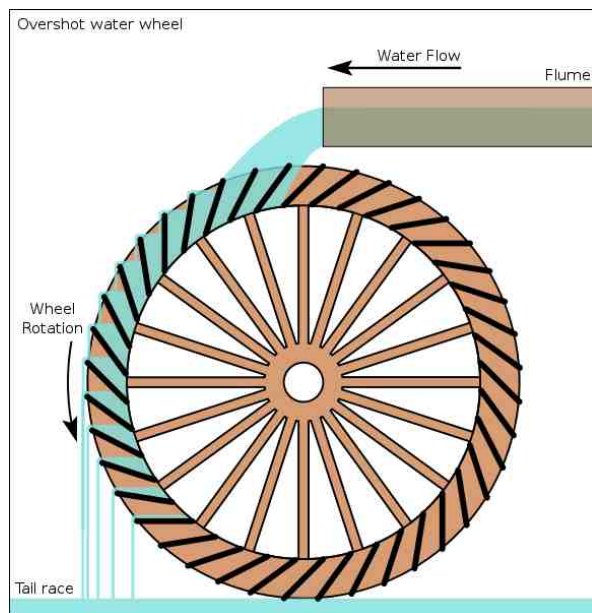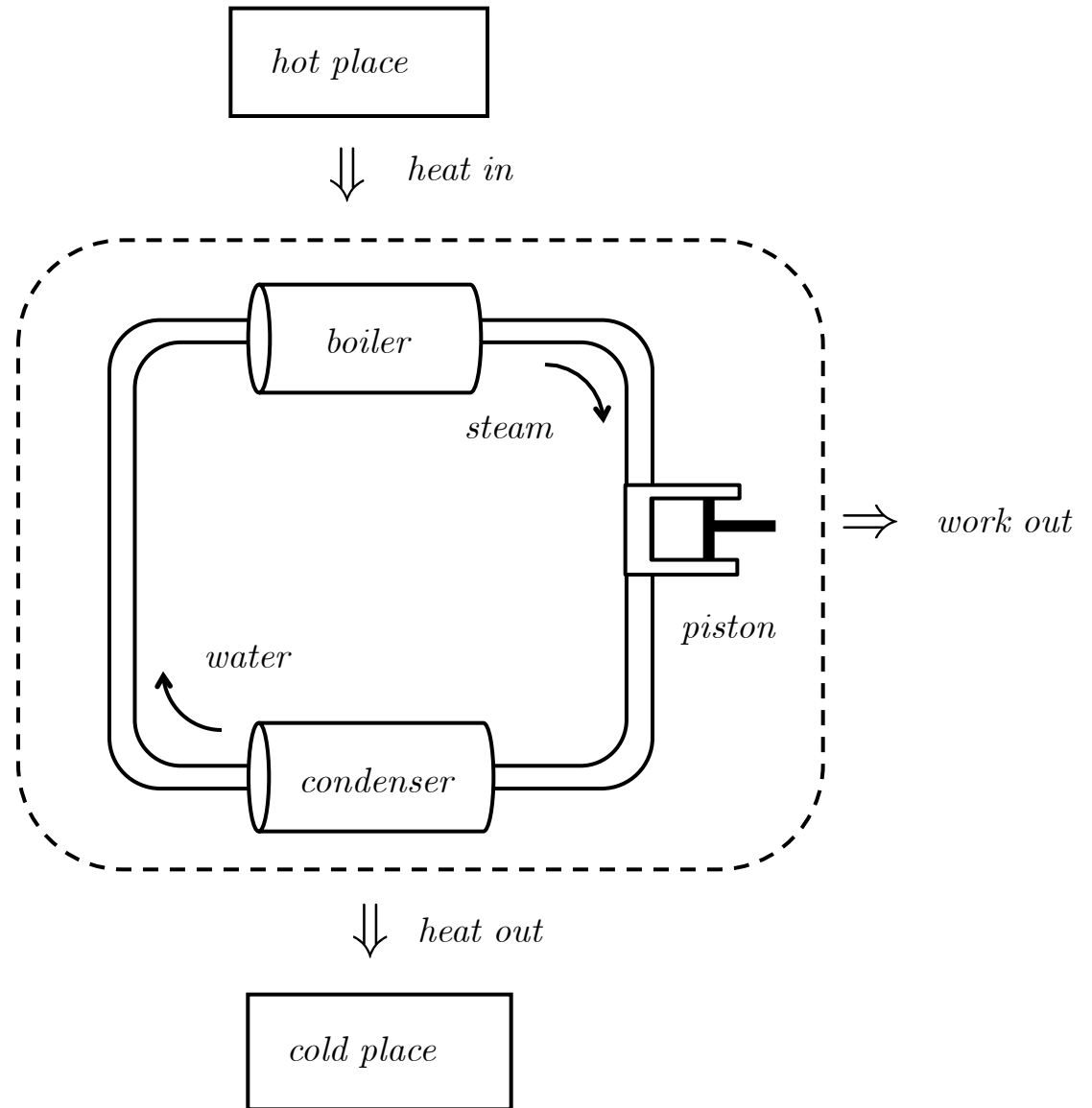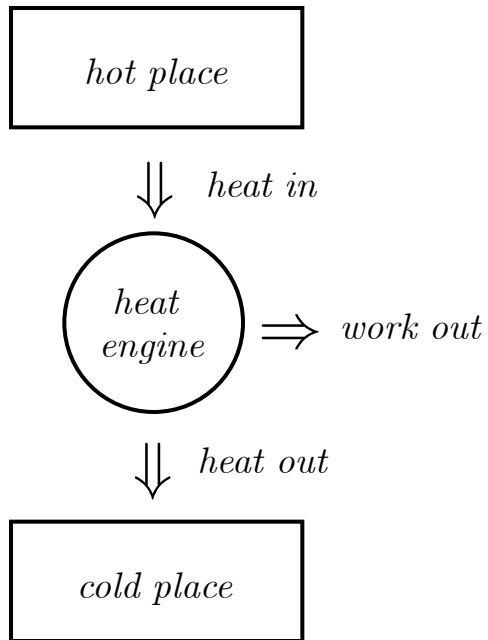
- Carnot, S. (1824) "Reflections on the Motive Power of Fire".

- _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

Overshot water wheel
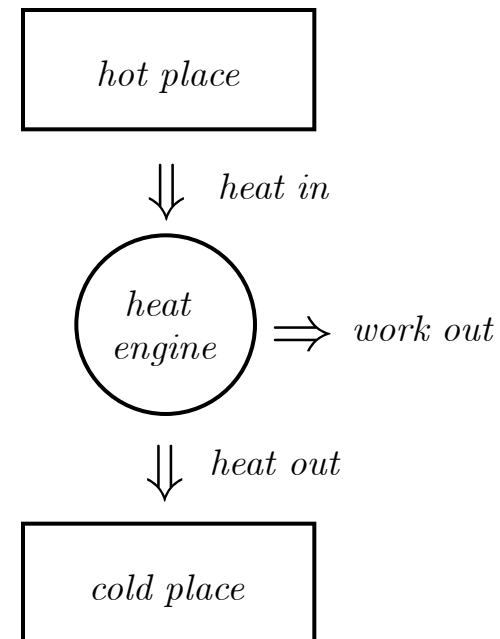
- Heat engine of economic interest: Steam engine!

hot place

⇓ *heat in*

heat engine ⇒ *work out*

⇓ *heat out*

cold place

hot place

⇓ *heat in*

boiler

steam

work out

piston

water

condenser

⇓ *heat out*

cold place

- James Watt (1765): Improvement in efficiency of Newcomen steam engine (addition of external condenser).
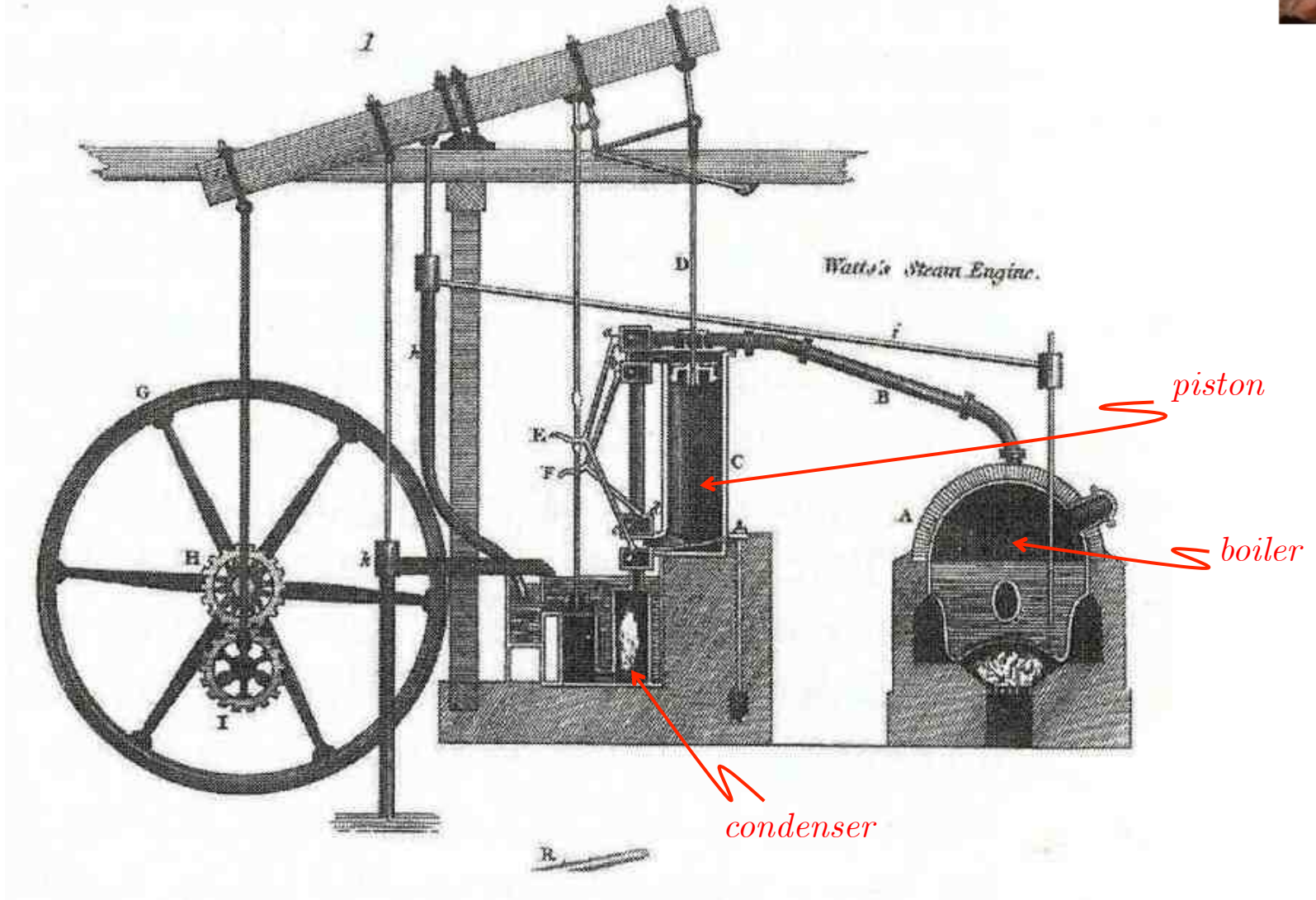
- *Important question*: What is the *maximally efficient* heat engine (*i.e.*, maximizes work output while minimizing waste)?

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

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

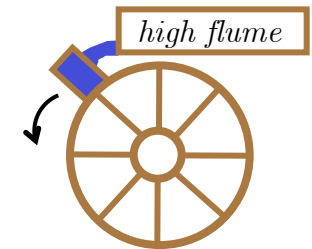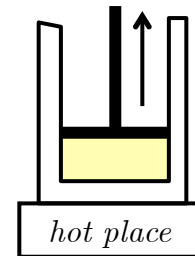*minimize splashing at high flume and low flume*
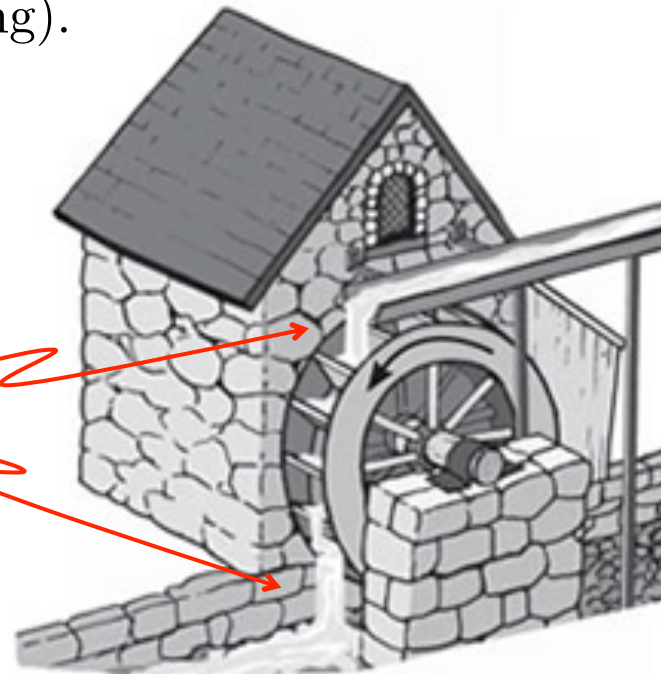
Carnot Cycle = One complete cycle of a maximally efficient heat engine.

Analogy: (temperature) ≈ (height); (heat) ≈ (water).

Step 1: _Isothermal (const. temp) expansion._

Heat absorbed at constant temp. Gas in
piston expands, doing work.
(Pressure decreases, volume increases.)

high flume

Step 2: _Adiabatic (const. heat) expansion._

Hot place removed. Gas expands at
constant heat, decreasing temp.
(Pressure decreases, volume increases.)

hot place
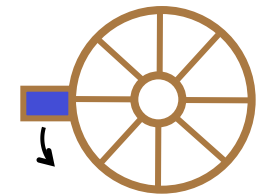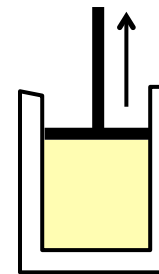
Step 3: _Isothermal contraction._
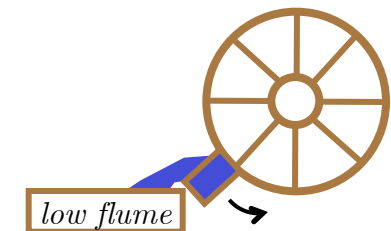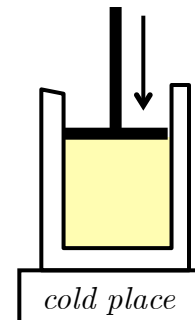
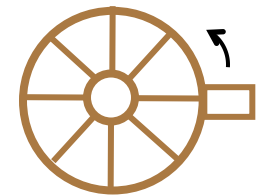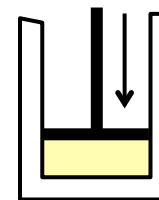_Heat shed at constant temp._ Gas contracts.
(Pressure increases, volume contracts.)

low flume

Step 4: _Adiabatic contraction._

Cold place removed. Gas contracts at
constant heat, raising temperature.
(Pressure increases, volume contracts.)

cold place

> *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 place; *not* on the working fluid.

Big Question: **What is the nature of heat?**

- *Carnot:* Implicitly adopts a substance theory of heat.

  - Heat is a substance (like water) called *caloric* that "falls" from
    hot places to cold places and in the process generates work.

  - *And*: *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

- 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.
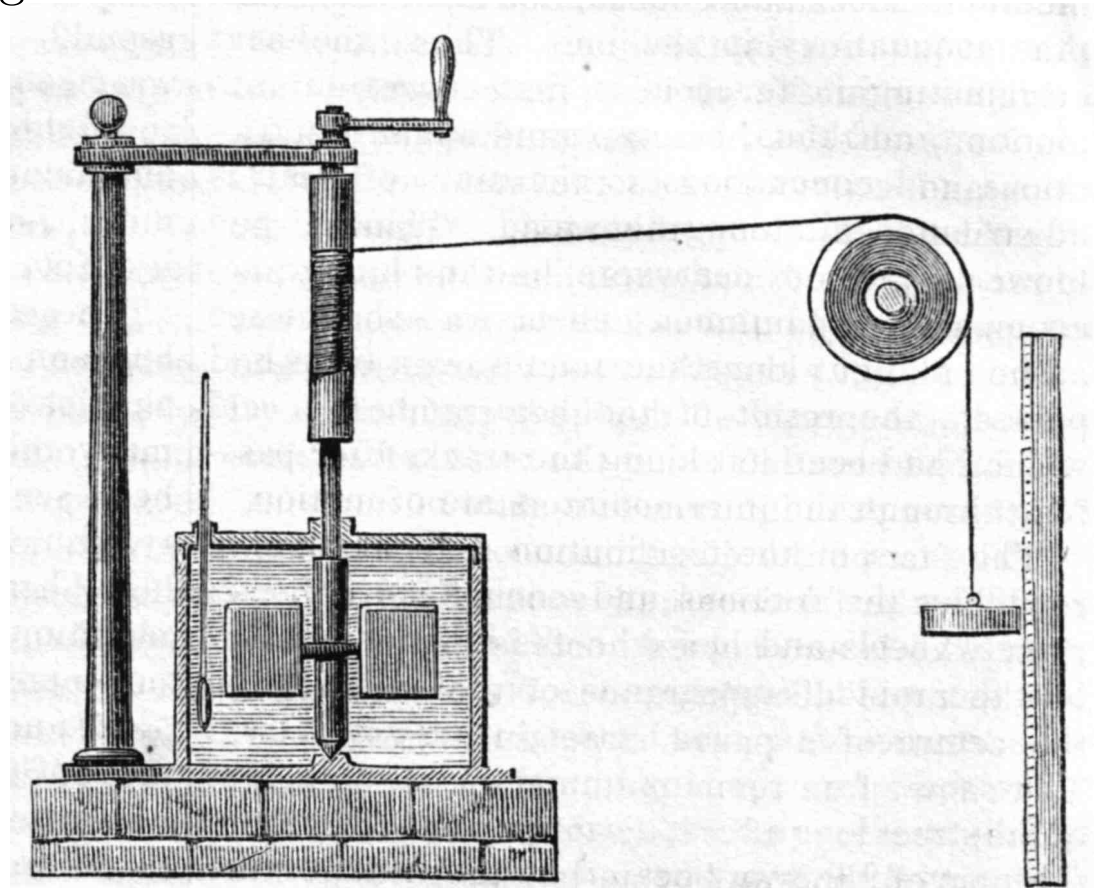
<u>*Two Key Results*</u>:

(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 (adiabatic) work required to take the water system between same two equilibrium states is independent of method used to generate it.
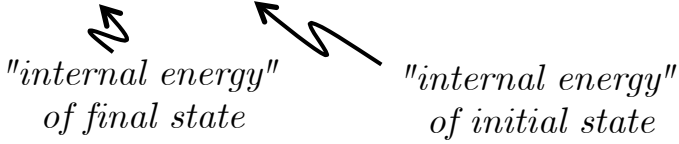
- Different weights, different drop heights.
- Use electric current instead of weights.

First Law of Thermodynamics:

If a thermally isolated system is brought from one equilibrium state to another, the work necessary to achieve this change is independent of the process used.

$$W_{Adiabatic} = U_2 - U_1 \equiv \Delta U$$

"internal energy"
of final state

"internal energy"
of initial state

If system is not thermally isolated:

$$\Delta U = W + Q$$

"heat" = non-mechanical exchange of energy between system and environment due to their temperature difference.

More generally:

1st Law states the conservation of energy:

- Many types of energy: work, heat, internal, kinetic, potential, chemical, electric, *etc.*

- *All* are interconvertible.

- For closed system: total initial energy = total final energy.

II. Formulations of the Second Law
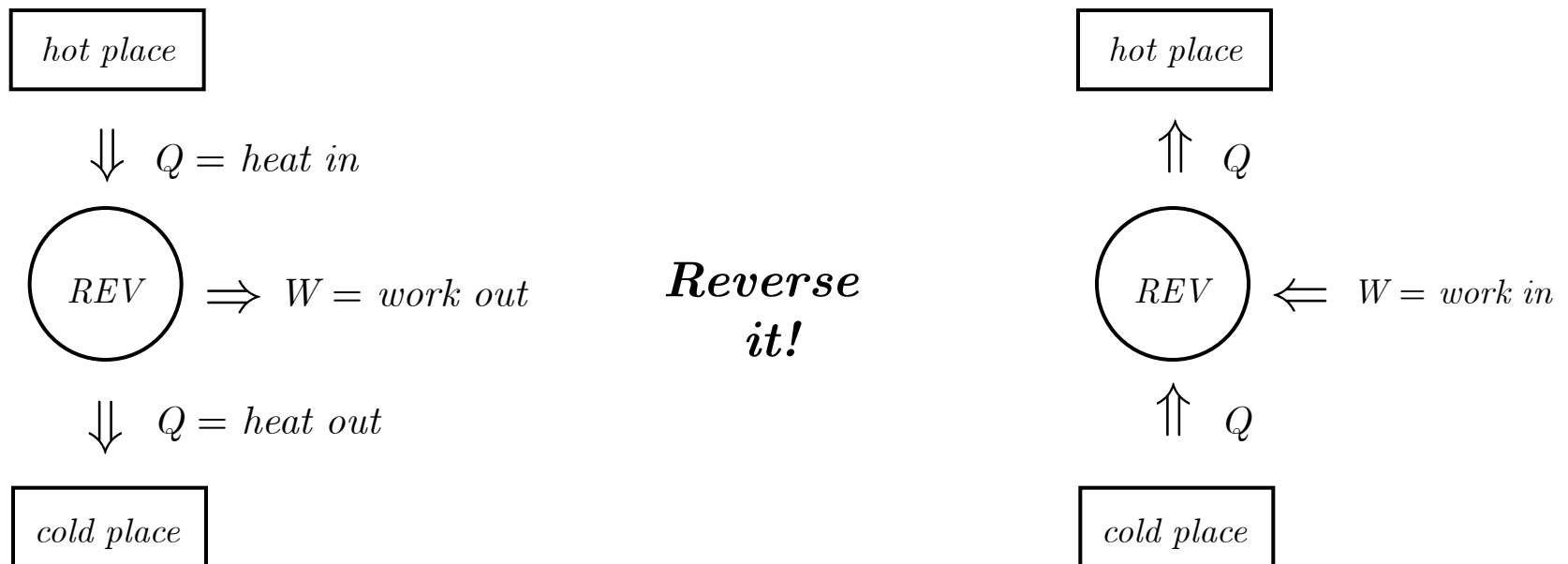
1. Thomson's (1849) "An Account of Carnot's Theory".

- *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)

- Call this a *reversible* heat engine.

hot place

$\Downarrow$ $Q = heat\ in$

(REV) $\Longrightarrow$ $W = work\ out$

$\Downarrow$ $Q = heat\ out$

cold place

Reverse it!

hot place

$\Uparrow$ Q

(REV) $\Longleftarrow$ $W = work\ in$

$\Uparrow$ 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.

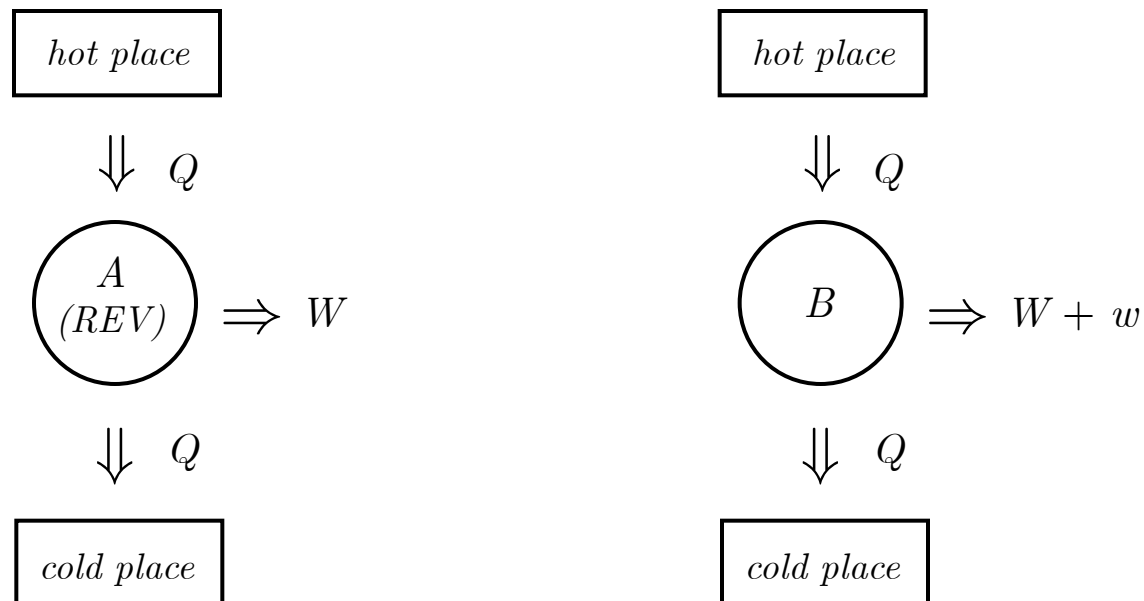|	
hot place	hot place
$\Downarrow Q$	$\Downarrow Q$
A (REV) $\Rightarrow W$	$B \Rightarrow W + w$
$\Downarrow Q$	$\Downarrow Q$
cold place	cold place

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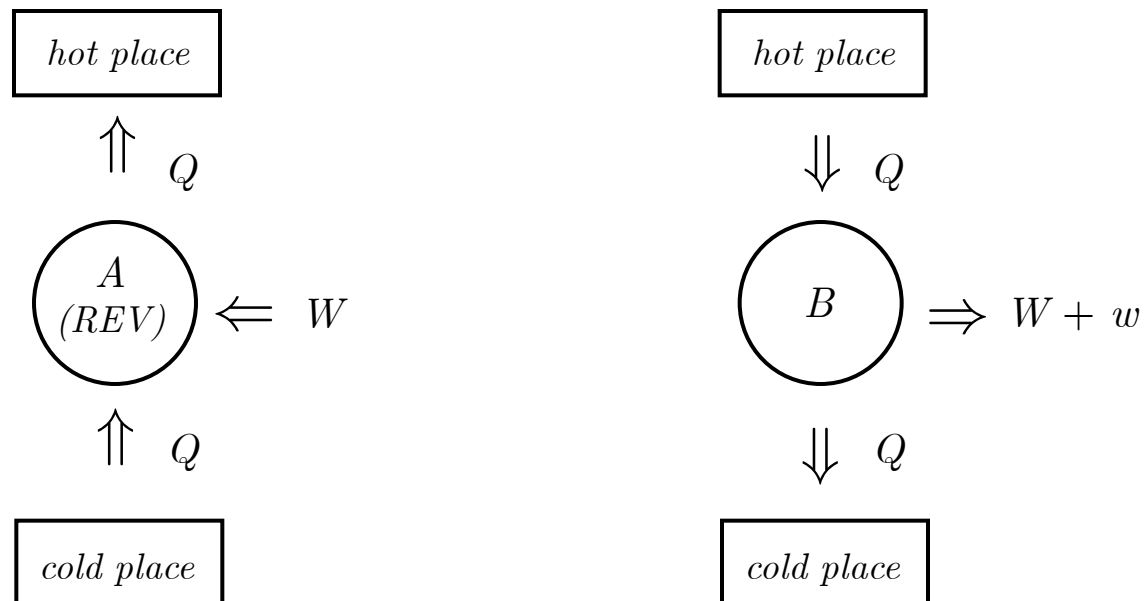
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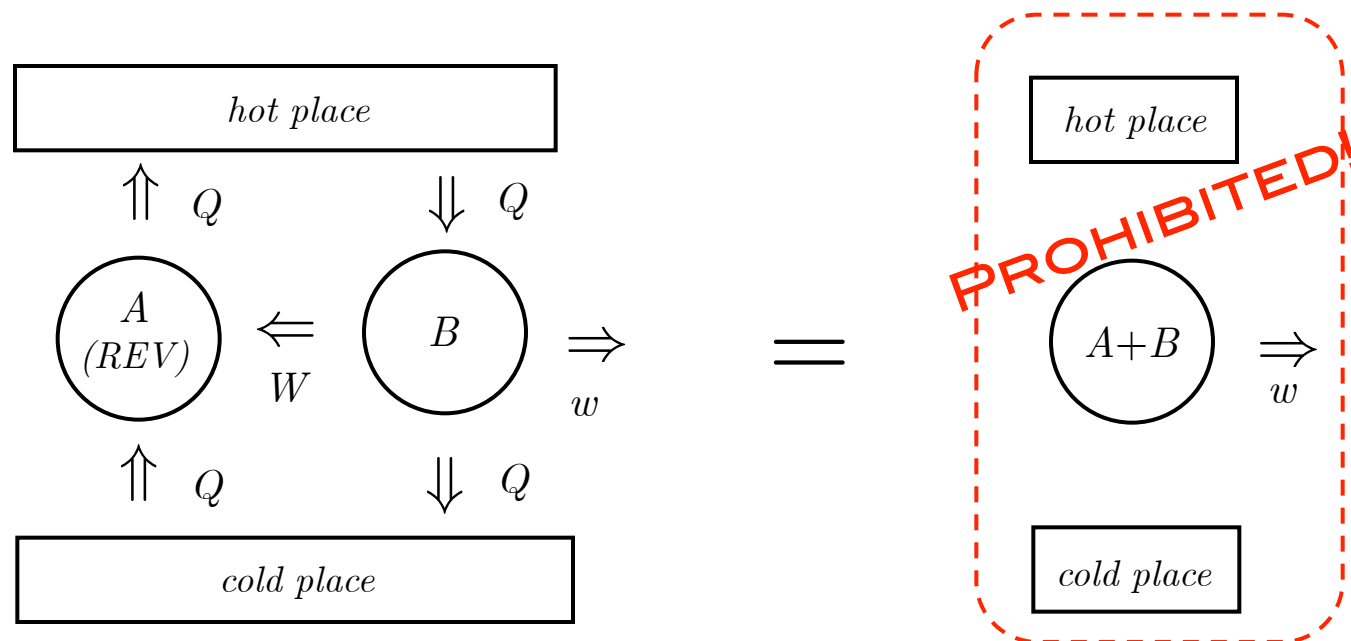
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- Now reverse A and hook it up to B.

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

2. 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

- *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).
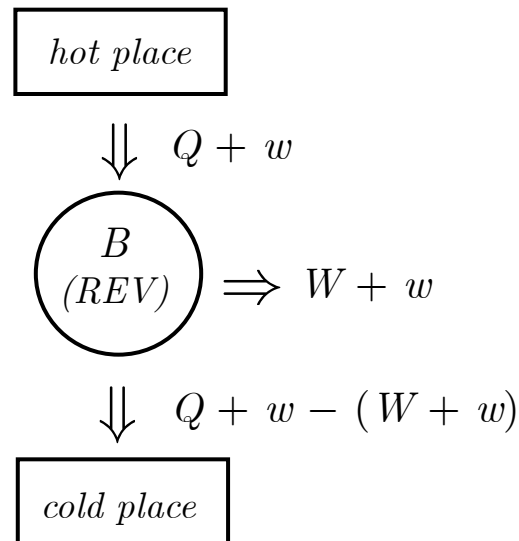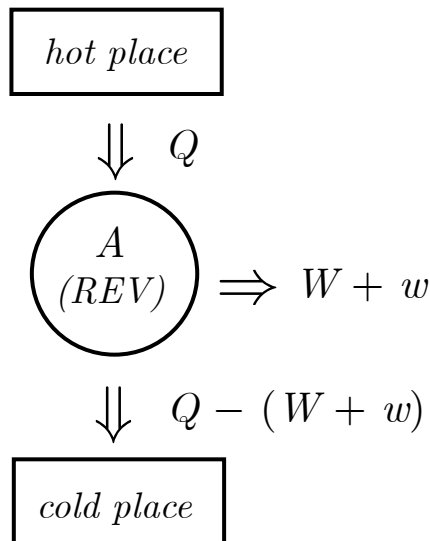
- *Consequences*:

  - 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 $Q_{out} = Q_{in} - W$.
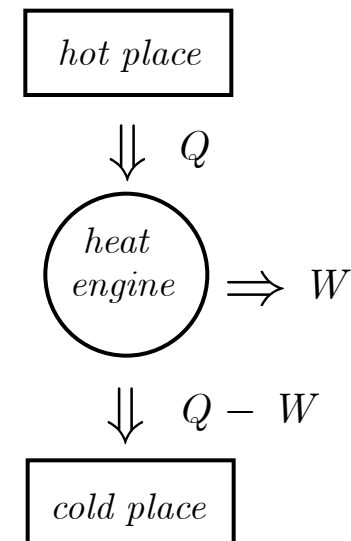
hot place

$\Downarrow Q$

heat engine $\Rightarrow W$

$\Downarrow Q - W$

cold place

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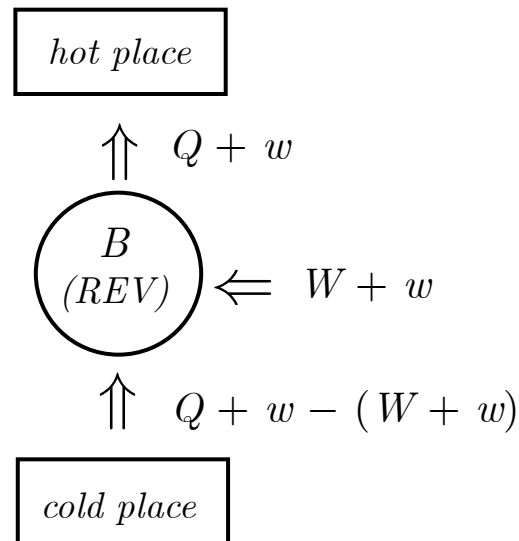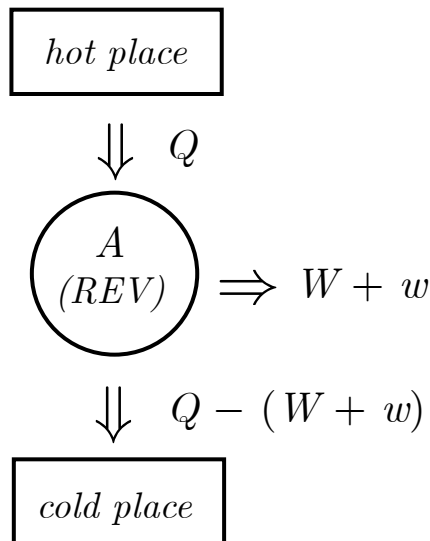
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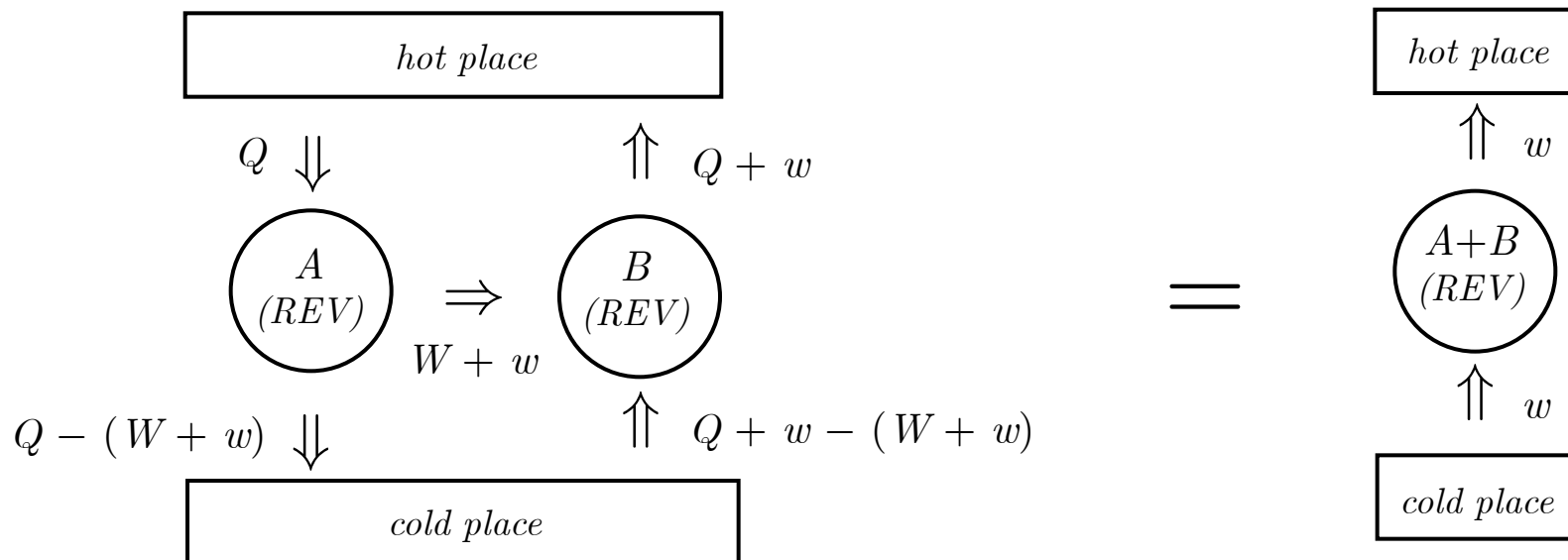
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- Engine $(A+B)$ takes an amount of heat w from a cold place to a hot place with no work input!

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- Clausius: 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."
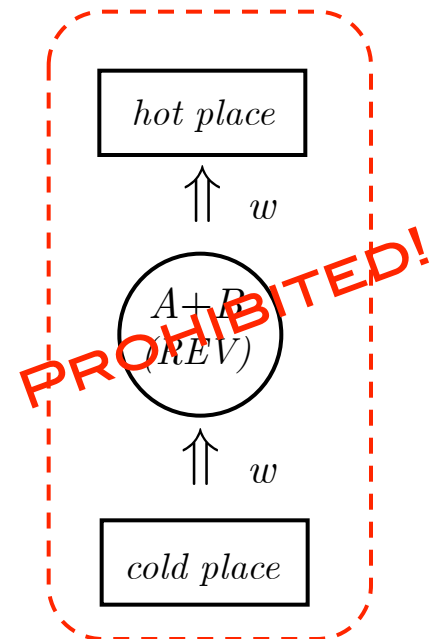
3. Thomson's (1851-55) "The Dynamical Theory of Heat"

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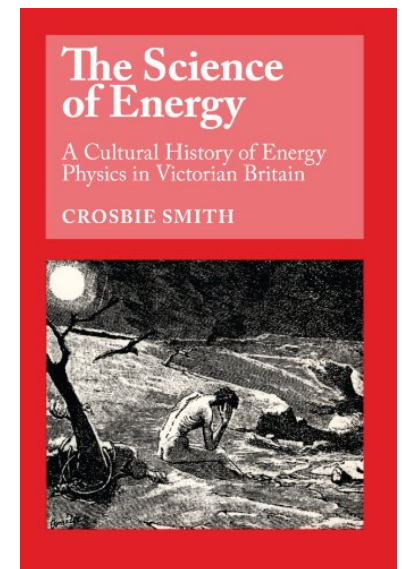
- *In other words (Carnot Claim #1)*: The most efficient heat engine for any given hot and cold places is a reversible heat engine.

- Thomson now seeks a theological and cosmological foundation for Prop. 2 (isn't satisfied with Carnot's or Clausius' reasoning).

- *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.*

The Science of Energy
A Cultural History of Energy Physics in Victorian Britain
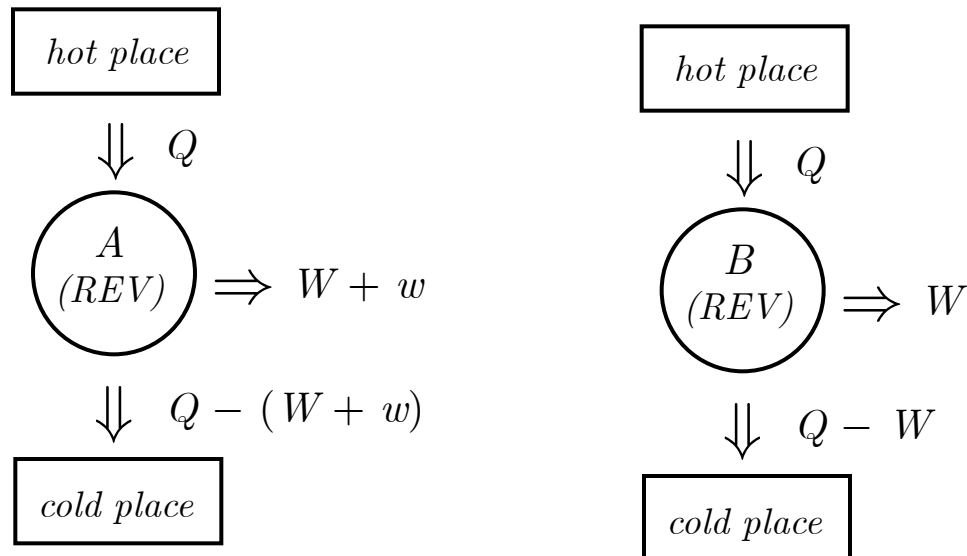CROSBIE SMITH

- *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).
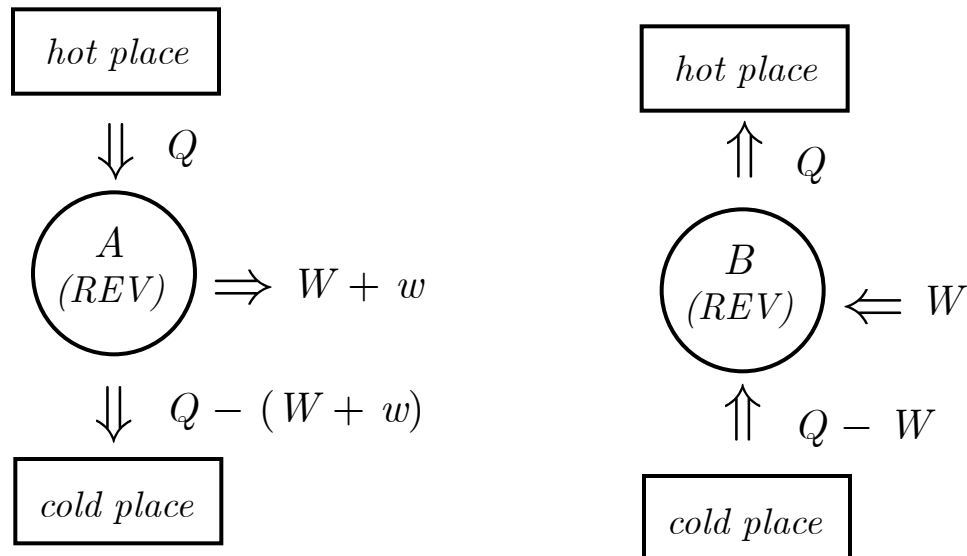
Thomson's Proof of Prop. 2

- 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.

hot place	hot place

$$\Downarrow Q \qquad\qquad\qquad \Downarrow Q$$

A (REV) $\Longrightarrow W + w$ $\qquad\qquad$ B (REV) $\Longrightarrow W$

$$\Downarrow Q - (W + w) \qquad\qquad \Downarrow Q - W$$

cold place	cold place

Thomson's Proof of Prop. 2

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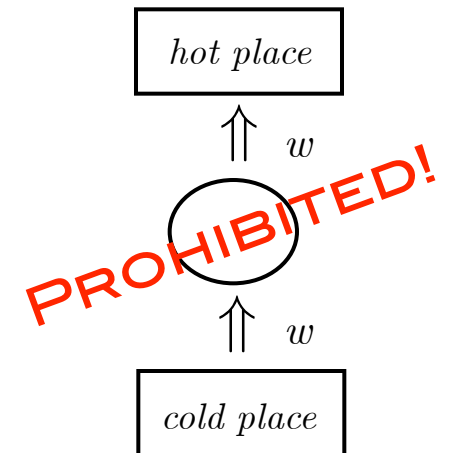
- Engine $(A+B)$ converts heat to work with no exhaust.
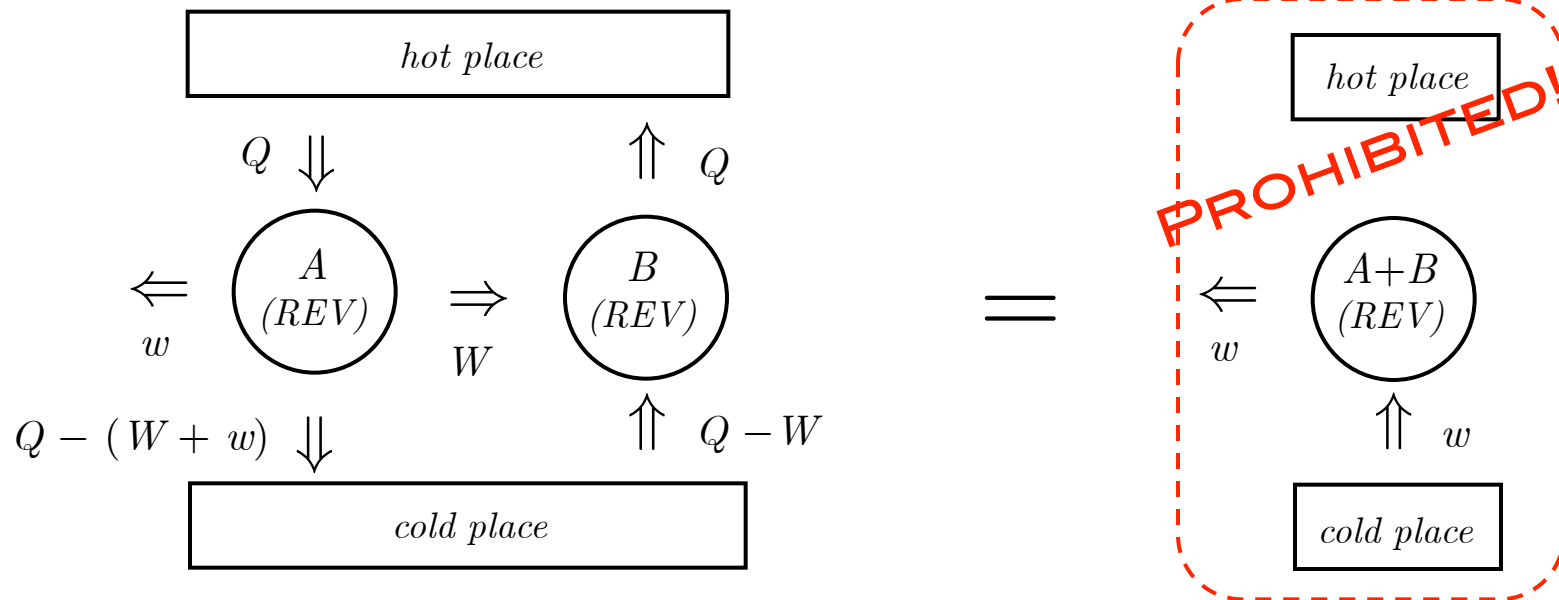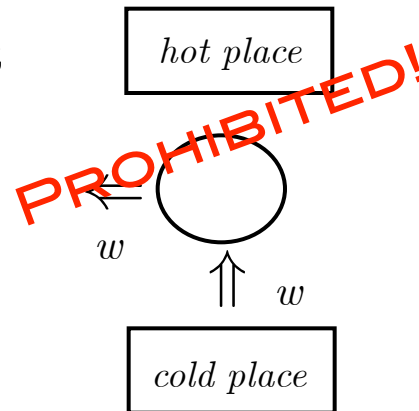
Three types of prohibited heat engines

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

hot place

PROHIBITED!

$\Rightarrow$ *w*

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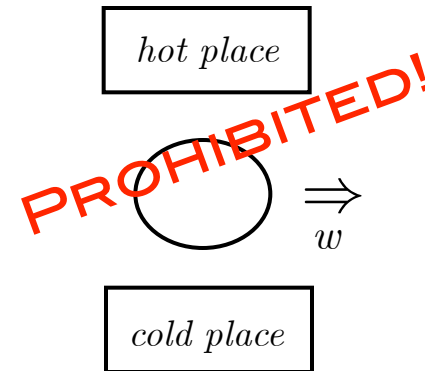
(b) *Clausius*: Heat transfer from cold to hot place with no work input:

hot place

$\Uparrow$ *w*

PROHIBITED!

$\Uparrow$ *w*

cold place

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

hot place

PROHIBITED!

w

$\Uparrow$ *w*

cold place

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