The Second Law of Thermodynamics

The first law of thermodynamics is not enough to describe all thermal phenomena.

There are many energetically allowed transitions that never happen.
For instance: hydrogen and oxygen mixtures do not convert to water without some trigger such as a spark.
This is because a certain activation energy is needed to start the reaction.

There are other phenomena however, which do not need any apparent activation energy and are possible, but do not happen.
For instance: a mixture of gases could separate into its components, but this never happens.

A simple expression from which quantitative progress could be made was needed:
this led to the Second Law of Thermodynamics

6.1 Statements of the Second Law

Clausius statement (from experimental evidence):

> It is impossible to construct a device that, operating in a cycle, produces no effect other than the transfer of heat from a colder to a hotter body.

heat cannot of itself flow from a colder to a hotter body

Kelvin-Planck statement:

> It is impossible to construct a device that, operating in a cycle, produces no effect other than the extraction of heat from a single body at uniform temperature and the performance of an equivalent amount of work.

heat cannot be completely converted into work without other effect

The Kelvin-Planck statement rules out
perpetual motion machines of the second kind,
which are those that live off stored thermal energy in the environment, converting it into work.

Such machines do not violate the first law
(conservation of energy),
but would nevertheless provide an endless supply of power
these are ruled out by the second law.

6.1.1 Conversion of work to heat

Work can be converted to heat

Examples:

- an electric kettle is an example of a device in which work is 100% converted into heat.
- in Joule's paddle wheel setup, the work of the paddle wheel is dissipated as heat, and this is true regardless of how hot the water is.

Therefore we can always assume that work can be dumped into a reservoir in a way entirely equivalent to heating it.

This is called irreversible work, in contrast, for example to storing the reversible work when one winds up a spring.

6.2 Heat engines

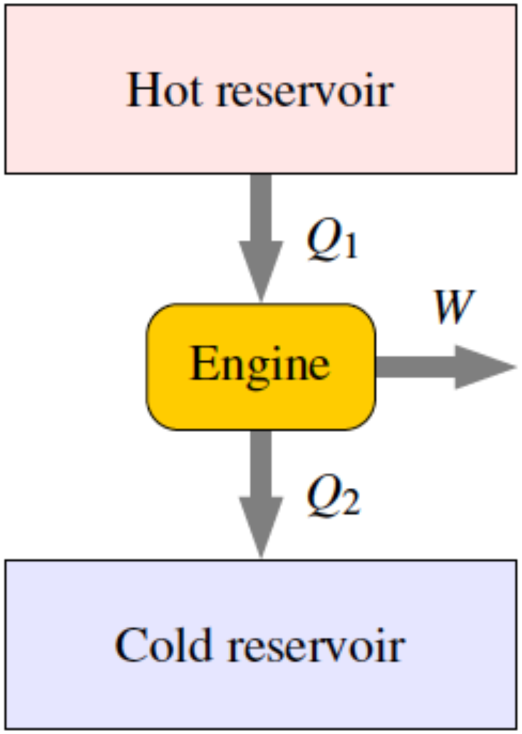
Much of the development of engines has been about making them more efficient.

A French engineer, Sadi Carnot, in 1824, clarified the idea of efficiency, and identified the simplest form of engine,
that we know as a heat engine.

A heat engine operates between two heat reservoirs, one hotter than the other.
You should think of the reservoirs as having such a large capacity that they don't change temperature as heat is taken from or added to them.
The reservoirs themselves are in equilibrium and therefore of uniform temperature.

The heat engine has the following key features:

1. It takes an amount of heat Q_1 from the hot reservoir.
2. It dumps an amount of heat Q_2 to the cold reservoir.
3. It performs an amount of work W
4. In doing the above, it completes one cycle, at the end of which it is in exactly the same state as it was at the start.



The last point is crucial, because it means that we do not have to worry about any change of internal energy of the engine

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The first law,
for a Carnot heat engine, becomes:

$$W = Q_1 - Q_2$$

Both a hot and cold reservoirs are needed for a heat engine!

When you sketch a heat engine,
always indicate the direction of the heat and work
because it defines the signs.

6.2.1 Efficiency of a Heat Engine

To rate an engine, we are interested in how much work can be obtained for a given amount of fuel.

The fuel heats the hot reservoir and is represented by Q_1.
So the efficiency of the heat engine is given by:

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

The smaller the amount of heat dumped to the cold reservoir, the more efficient the engine.

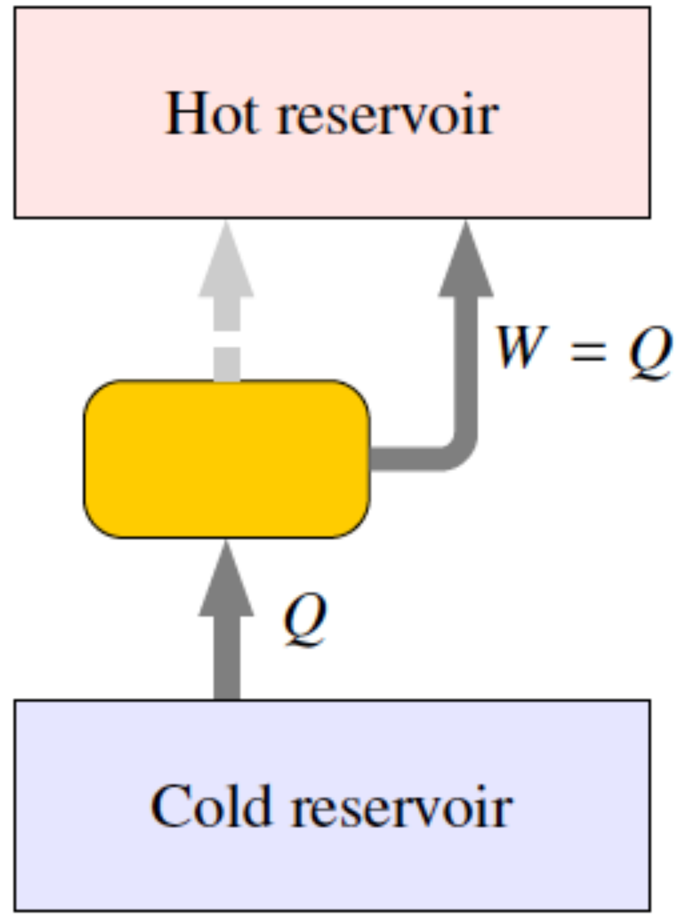
A major result of thermodynamics is that we will be able to place an upper limit on this efficiency, and this upper limit is a function only of the temperatures of the reservoirs.

6.2.2 Equivalence of the Clausius and Kelvin-Planck Statements

Let us consider a hypothetical device that can convert heat completely into work

heat Q is extracted from a cold reservoir and converted into work so that W = Q. The dashed line is an indication that no other heat is transferred. Work is being directed into a hot reservoir.

The whole process violates the Clausius statement, because we have transferred heat Q from the cold reservoir to the hot reservoir with no other effect



the hypothetical engine that
can convert heat completely into work
cannot exist

it is not possible to make an engine which
fully converts heat into work
without other effect

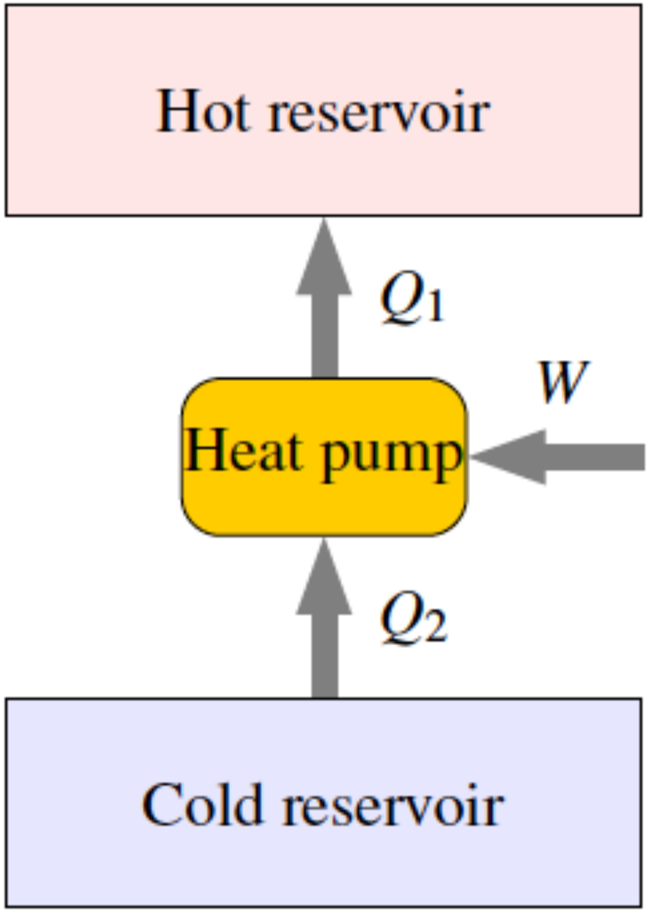
the Clausius statement
implies
the Kelvin-Planck statement of the second law

6.3 Heat pumps and refrigerators

If we run a heat engine backwards we have device known as a heat pump

a device which when work W is performed on it, extracts Q_2 from a cold reservoir and dumps Q_1 to the hot reservoir

$$Q_1 = Q_2 + W.$$



One can think of the hot reservoir as a house to be heated, while the cold reservoir is a nearby stream.

For every W of work done to run the heat pump (usually electrical),

one obtains W + Q_2 of heating.

The efficiency of a heat pump is defined as: $$\eta_{\mathrm{HP}} = \frac{Q_1}{W}$$

If the cold reservoir is an insulated box,
the hot reservoir is the room the box is in,
we have a refrigerator or freezer.

In this case one is interested in the amount of cooling per unit work, so the refrigerator efficiency is:

$$\eta_{\mathrm{R}} = \frac{Q_2}{W}$$

6.4 Carnot's theorem

Carnot focused upon the idea of a reversible engine

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a reversible engine is one in
which every part of its cycle is thermodynamically reversible

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to draw the engine in reverse, one only needs to
reverse the directions of the arrows,
but the numerical values of Q_1, Q_2 and W are unchanged

Carnot's implementation of a reversible engine is called a
Carnot cycle

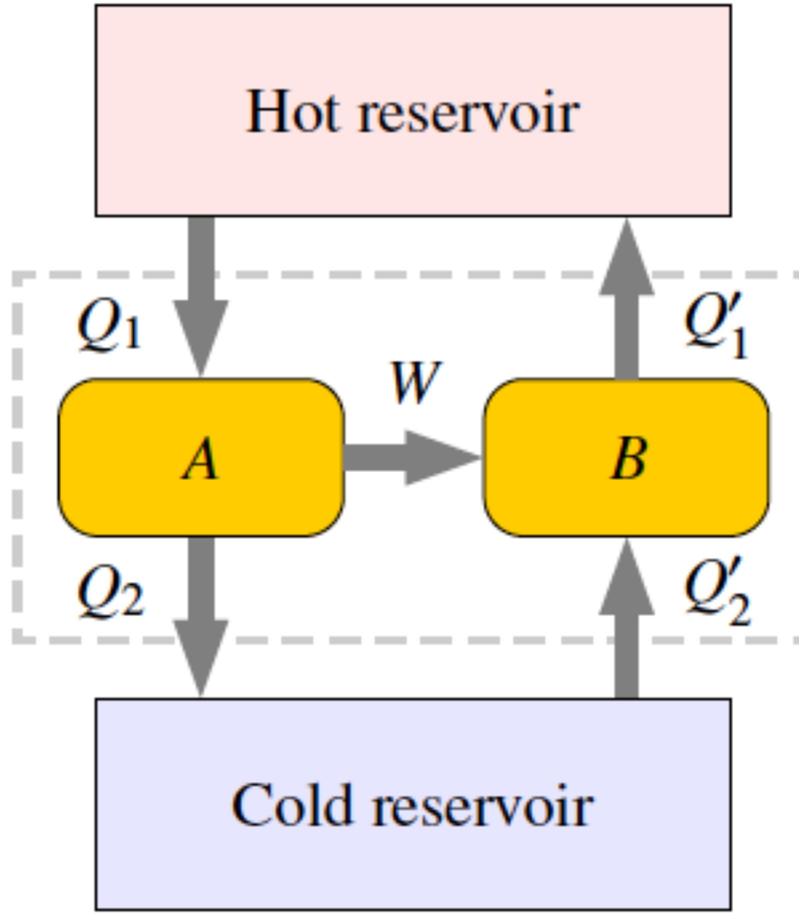
Carnot's theorem says that
reversible engines are the most efficient of all.

Let us consider two engines, A and B.

Engine B is reversible and is run as a heat pump using the power generated by engine A, which may or may not be reversible.

Carnot's theorem states that

$\eta_B \geq \eta_A$



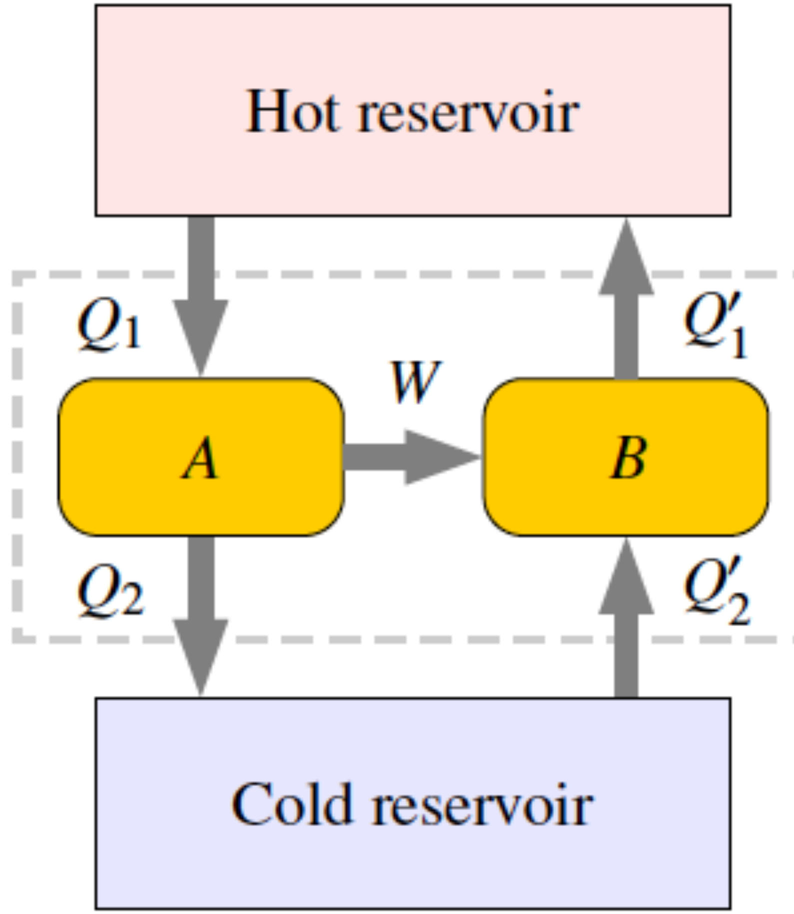
Since B is reversible: $\eta_B = \frac{W}{Q'_1}$

the magnitudes of Q'_1 and Q'_2 remain the same through the switch from engine to heat pump

The efficiency of engine A is:

$$\eta_A = \frac{W}{Q_1}$$

All the work produced by A is used to run B, thus the two engines form a complete system (indicated by the dashed box) which produces no work but just transfers heat from one reservoir to another



By the Clausius statement of the 2nd law,
the heat must flow from the hot to the cold reservoir:

$$Q_1 - Q_1' \geq 0$$

$$\Downarrow$$

$$Q_1 \geq Q_1'$$

$$\Downarrow$$

$$\frac{W}{Q_1} \leq \frac{W}{Q_1'}$$

$$\Downarrow$$

Carnot's theorem $$\boxed{\eta_A \leq \eta_B}$$

Had A been reversible, we could have reversed the argument to show that $\eta_B \leq \eta_A$

For both to be correct, we must have $\eta_B = \eta_A$.

Therefore we now know that reversible engines are the most efficient of all engines,
and that all reversible engines, operating between the same reservoirs, have the same efficiency

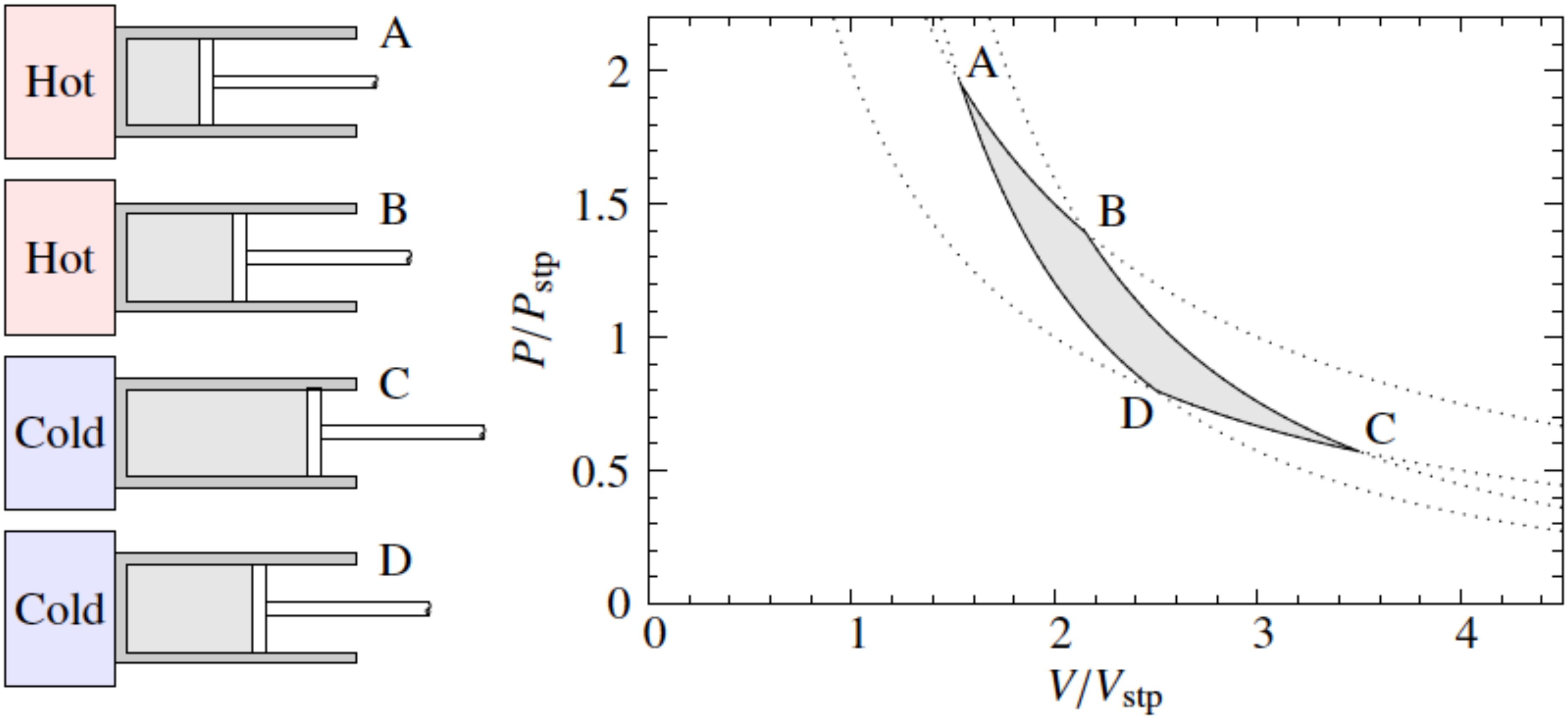
one only needs to conceive of one reversible engine to know the efficiency of them all.

6.5 The Carnot cycle

Let us consider an engine that operates in a cycle of four reversible steps, which together are known as the Carnot Cycle.

The Carnot cycle is based upon the expansion and compression of an ideal gas.

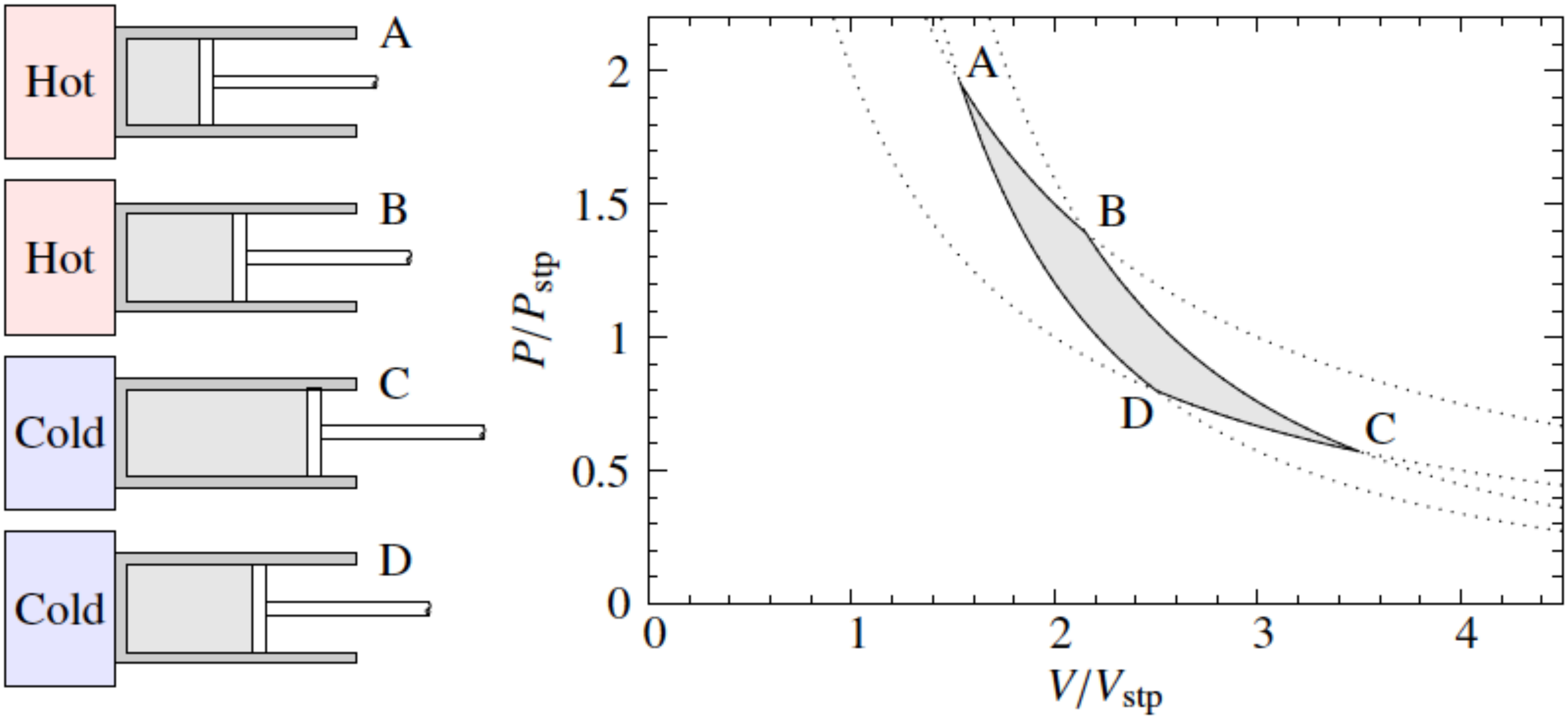
Remember that we are free to choose as simple a system as possible, because Carnot's theorem shows that all reversible heat engines, operating between the same reservoirs, have the same efficiency.



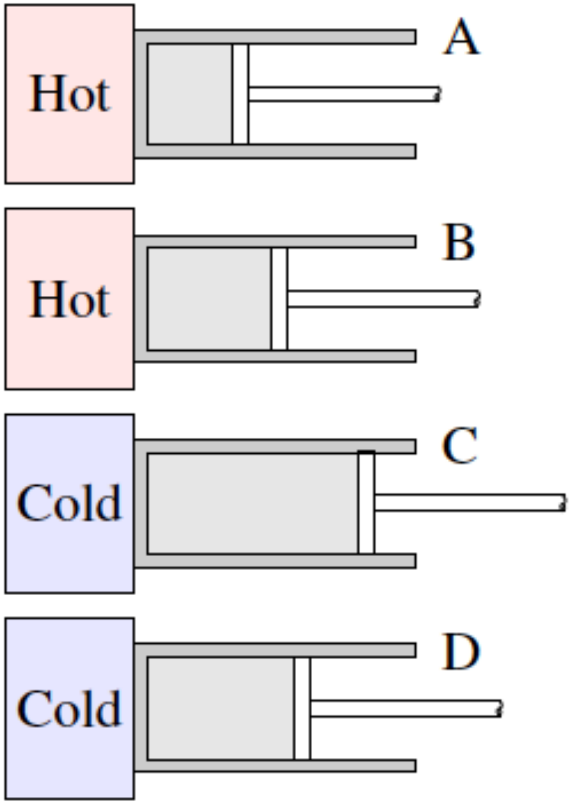
We start with the gas in thermal contact with the hot reservoir, at a point labelled A

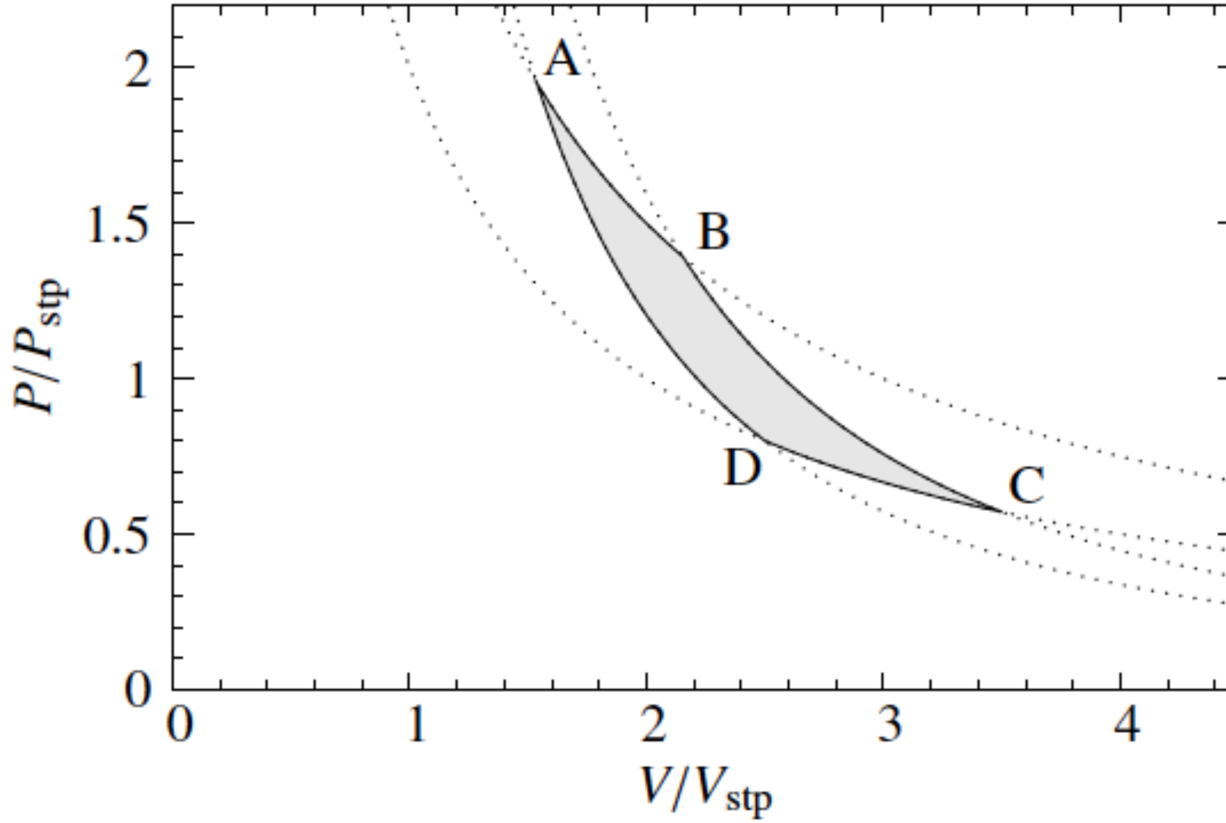
- $A \rightarrow B$

  While in contact with the hot reservoir, the gas is expanded isothermally, doing work W_1 while absorbing heat Q_1. As it is ideal, $U = U(T)$, so $\Delta U = 0$. Therefore $W_1 = Q_1$ (NB: W_1 here defined as work done *by* the gas, not on it).



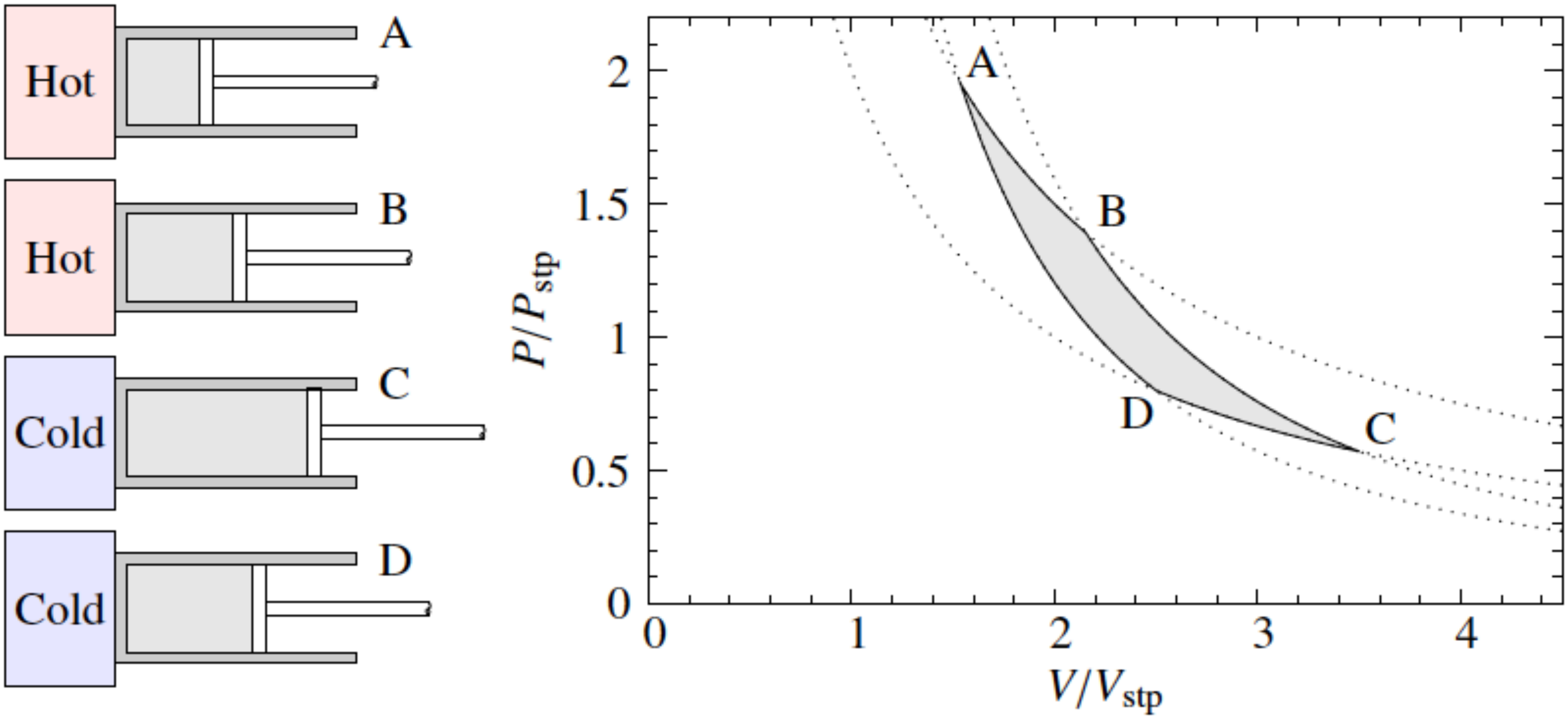
- B → C
  The gas is removed from contact with the hot reservoir and expanded adiabatically until it is in thermal equilibrium with the cold reservoir (its temperature drops during adiabatic expansion). During the expansion it performs work W_2, while $Q = 0$. Therefore $\Delta U_2 = -W_2$.





- C → D

  The gas is placed into thermal contact with the cold reservoir and isothermally compressed. Work W_3 is done on the gas during the compression, and it gives up heat Q_2 to the cold reservoir. As in step 1, $\Delta U = 0$, so $Q_2 = W_3$.



- D → A
  Finally the gas is removed from thermal contact with the cold reservoir and adiabatically compressed until it is once more in thermal equilibrium with the hot reservoir, and it has the volume that it started with. Work W_4 is done on the gas during this stage, while $Q = 0$, so $\Delta U_4 = W_4$.

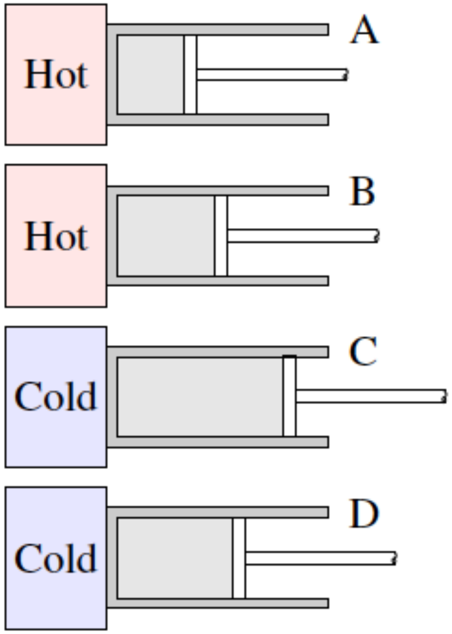
The end result is that the gas has completed a cycle, ending in the same state as it started.

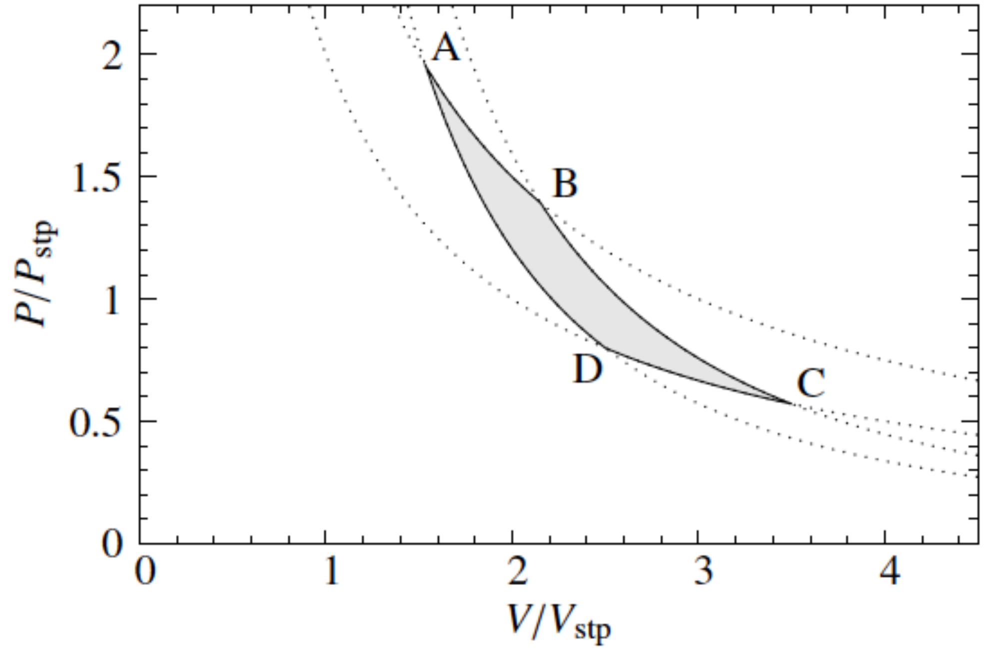
Q_1 has been extracted from the hot reservoir,

while Q_2 has been dumped to the cold reservoir,

and the net work extracted is:

$$W = W_1 + W_2 - W_3 - W_4 = Q_1 - Q_2$$





- Since areas in indicator diagrams represent work, the shaded area is the work extracted from one cycle of the Carnot cycle.

- The two lines representing the adiabatic changes, PV^{γ} = constant rise more steeply than those representing the isothermal changes, PV = constant

- Isotherms cross the adiabatics, but isotherms do not cross each other, nor do adiabatics.
  This should be obvious for isotherms since the same state cannot have two different temperatures.

6.6 Summary

- We need more than just the First Law of thermodynamics to describe the thermal behaviour of matter.

- There are some processes possible under the First Law which nevertheless never happen.

- The Second Law (in the form proposed by Clausius) is a statement of one such impossible process,
  the spontaneous transfer of heat from a cold to a hot body.

- This also leads to an equivalent statement to the effect that heat cannot be turned completely into work.
  The equivalence was established through the idea of a heat engine.

- Further the second law applied to such engines was used to establish that thermodynamically reversible engines are the most efficient

- All reversible engines running between the same reservoirs have the same efficiency.