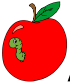
PREVIOUSLY ON ...*Thermodynamics*

First Law - Energy is Conserved

Sometimes redefine "energy" so that First Law is true.

$$\mathrm{dU} = đQ + đW$$

Combined, Work and Heat have the same effect



Add two inexact differentials - get an exact one

Two heat capacities (at least) $C_v = \left(\frac{\partial U}{\partial T}\right)_V$; $C_P = \left(\frac{\partial H}{\partial T}\right)_P$

Enthalpy: H= U+PV. For pressure boundary conditions

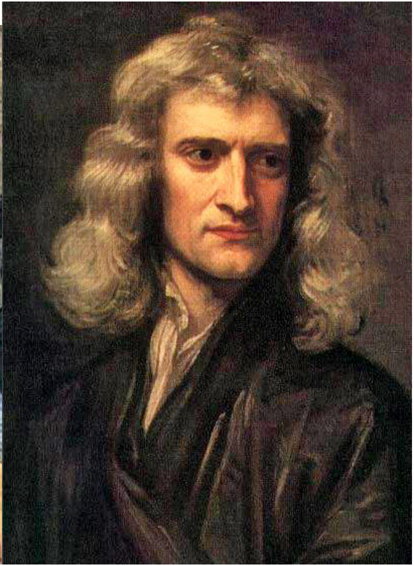
Adiabats: How c_P and c_V get into the exponent PV^γ

Free expansion (Joule); Constant U

Does "Irreversible" mean "Friction" ?

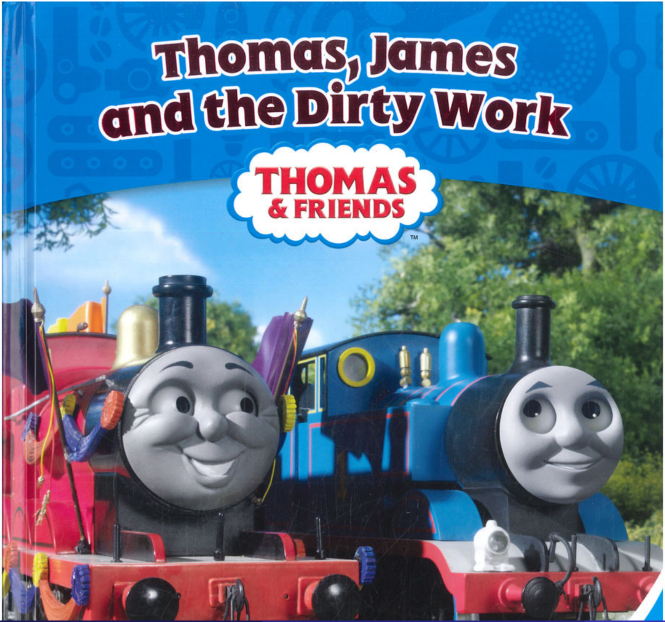
- Irreversibility defines time itself (but not units)
- First Law - Work + heat equivalent - *time reversible*
- Friction - Work done becomes heat - *irreversible*
- Dissipation - Work done becomes heat - *irreversible*
- Joule's paddle wheel - Work done becomes heat - *irreversible*
- Does irreversibility mean that work/motion always turns into heat?
- Everything tends to a natural state of rest *Aristotle*
- Unless it has *Qi* or Vitalism.

Ancient wisdom

Ask an 70-year old expert in work...

"No" say the Engines



Carnot's theorem

No engine operating between two reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.

"Reflections on the Motive Power of Fire" by Sadi Carnot

Je suis le meilleur qu'il peut y avoir.

Cyclic processes - Carnot cycle and engine

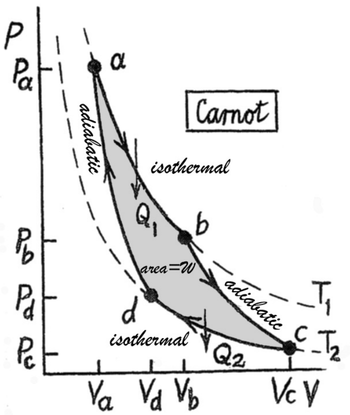
A *cyclic* process:

- **system** returns to initial equilibrium
- **surroundings** change
- **work** is done

All processes quasistatic/reversible.
During the cycle the values of the state variables change, system exchanges heat and mechanical energy with its surroundings.

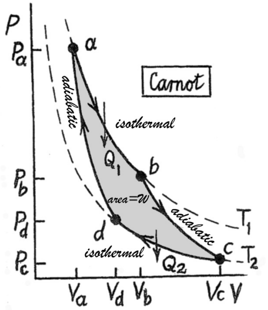
e.g. Carnot cycle:

1. isothermal expansion,
2. adiabatic expansion,
3. isothermal compression,
4. adiabatic compression.



The Carnot cycle and engine

Surroundings:
Two constant temperature heat reservoirs,
Pistons moving in all processes
Heat is only exchanged along the two isotherms
Work done $= \oint PdV =$ area inside the closed curve.

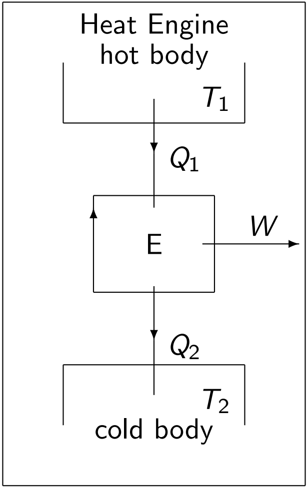


In each cycle, heat $Q_1 - Q_2$ enters and work W is delivered.
Illustrates general principles of heat engines.
Heat pumps and refrigerators are similar, using work to move heat from cold to hot.
System is a fluid known as the **working substance**.

The efficiency of a heat engine

A schematic of a general engine.

Q_1, Q_2 and W are heat in, heat out and work done **by** the working substance.
Work done **on** the working substance is $-W$



First Law for each complete cycle:

$$\Delta U = Q_1 - Q_2 + (-W) = 0$$

From this, $W = Q_1 - Q_2$, and the efficiency η of the engine is given by

$$\boxed{\eta = W/Q_1 = 1 - Q_2/Q_1}$$

Power = Work per cycle $\times$ cycles per second.

Working substance doesn't affect efficiency

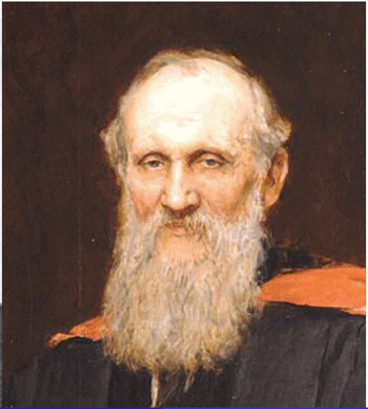
$$\boxed{\eta = W/Q_1 = 1 - Q_2/Q_1}$$

- No mention of working substance!
- Efficiency depends only on the heat flows.
- Working substance does affect design of the engine.
- Can run the engine "backwards":
  put work in and move heat from cold to hot.
- Reversed engine is a refrigerator or heat pump.

Efficiency is "Energy you get out in" divided by "Energy you put in".
This is *different* for engines, fridges and heat pumps.

The Second Law of Thermodynamics

- Defines processes which can never occur even though they are energetically possible.
- Use heat engines to help visualise these processes.
- There are two statements of the second law, one by Clausius, and the other by Kelvin, modified by Planck.

Clausius and Kelvin Second Law

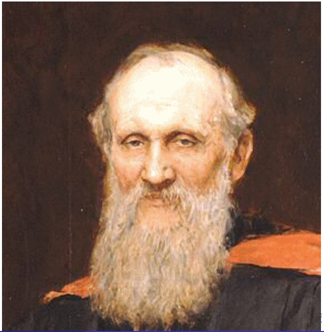
It is impossible to construct a device that, operating in a cycle, produces no effect other than...

The Clausius statement:

... the transfer of heat from a colder to a hotter body

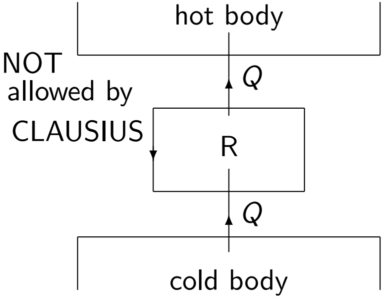
The Kelvin-Planck statement

... the extraction of heat from a single body at a uniform temperature and the performance of an equivalent amount of work.

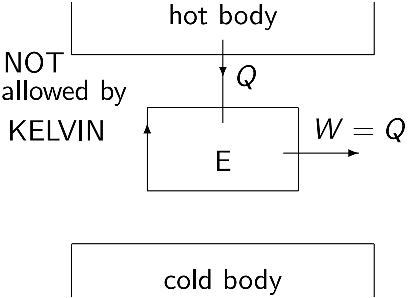


Clausius and Kelvin Second Law

“R”: forbidden refrigerator.



“E” forbidden engine.



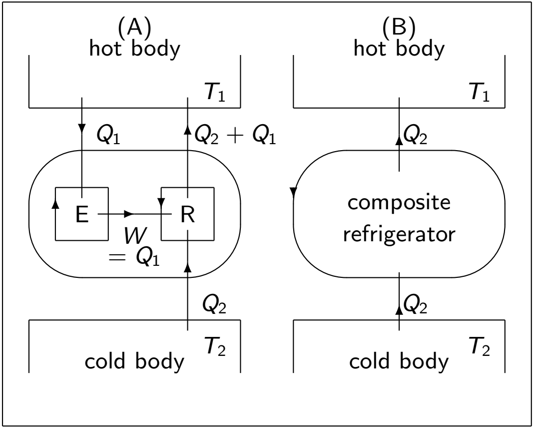
n.b. *Body* rather than *heat reservoir*:
meaning the transfer of heat can change the temperature.

Equivalence of Clausius and Kelvin-Planck statements

Proved by showing that if either statement is false, so is the other.
Suppose Kelvin-Planck is false.

KP-violating Engine (E) runs refrigerator (R).
R extracts Q_2 from the cold body, delivers $Q_1 + Q_2$ to the hot body (1[st] law).

E+R can be treated as a composite refrigerator.
E+R transfers heat Q_2 from a colder to a hotter body.



E+R violates Clausius's statement.

Heat and work are considered per cycle in this argument.

The Carnot cycle and engine

Surroundings:
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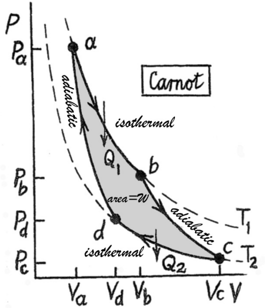

In each cycle, heat $Q_1 - Q_2$ enters and work W is delivered.
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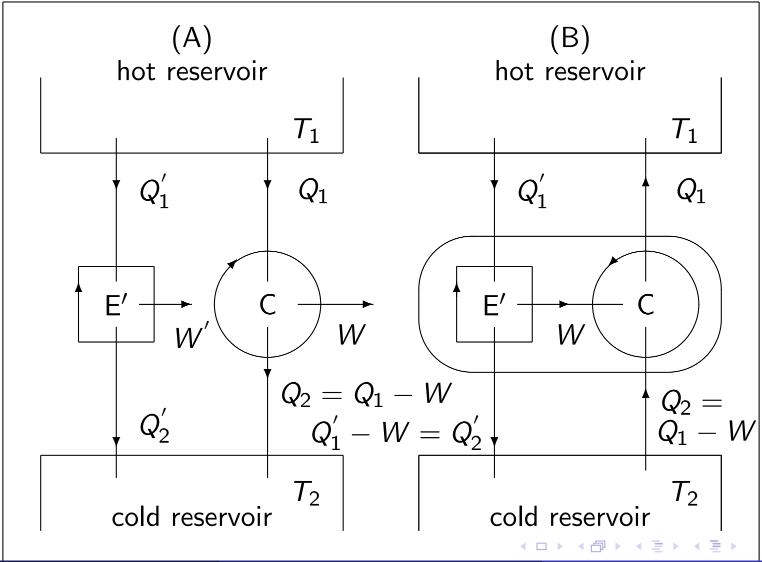
Carnot's theorem and a corollary

Carnot's theorem proved using Clausius Statement.



Proof that Carnot's theorem is equivalent to Second Law

- Consider a Carnot-violating engine E$'$ (efficiency η') and a Carnot engine C (efficiency η_C) operating between the same heat reservoirs.
- Assume the engines do equal Work (W'=W)
- Carnot engine is reversible, so it can be driven backwards.
- **Assuming** $\eta' > \eta$, $W'/Q_1' = W/Q_1' > W/Q_1$ **leads to** $Q_1 > Q_1'$.
- Use C to drive E'.
- $C + E'$ is a refrigerator which moves heat $Q_1 - Q_1'$ from cold to hot reservoir *without external work*.
- This contradicts Clausius's statement of the 2$^{\text{nd}}$ law.
- So the assumption $\eta' > \eta_C$ cannot be valid.

If $\eta' = \eta_C$, then $Q_1' = Q_1$: heat flows are zero and no net work. The efficiency η for any real engine must therefore satisfy

$$\boxed{\eta \leq \eta_C}$$

Corollary 1: Efficiency depends on temperature

Consider compound device based on two Carnot engines, C_a and C_b, with efficiency η_{c_a}, η_{c_b}.

- If C_a drives C_b backward, Carnot's Theorem: $\eta_{c_a} \leq \eta_{c_b}$.
- However, for C_b driving C_a backwards, $\eta_{c_b} \leq \eta_{c_a}$.
- The only option is $\eta_{c_a} = \eta_{c_b}$,

hence the corollary:

> *All Carnot engines operating between the same two reservoirs have the same efficiency (INDEPENDENT of the working substance).*

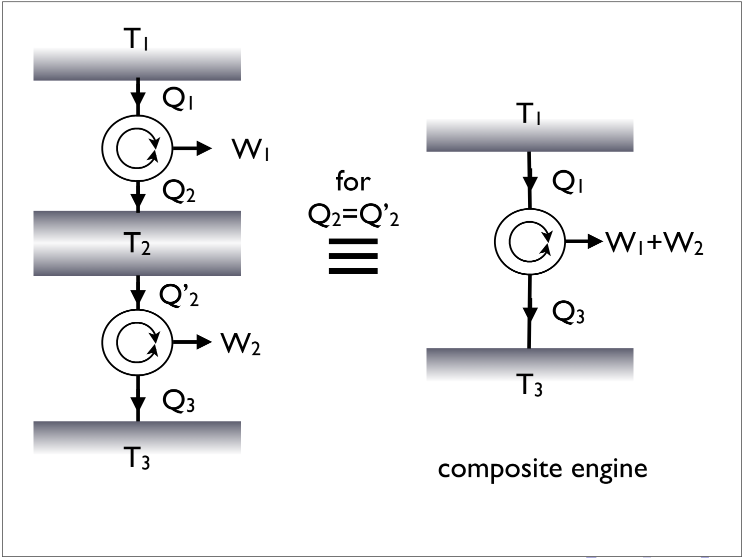
Corollary 2: Existence of thermodynamic temperature

- Thermodynamic efficiency of any *reversible* heat engines operating between the *same* two temperature reservoirs is equal.
- Efficiency, $\eta_R = 1 - \frac{Q_2}{Q_1}$, can only depend on reservoir temperatures.
- Ratio Q_1/Q_2 is therefore some universal function T_1 and T_2:

$$Q_1/Q_2 = f(T_1, T_2)$$

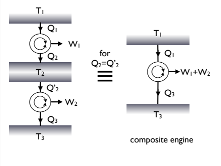
Next, show $f(T_1, T_2)$ is a product of functions of one temperature $\theta(T)$. Consider a composite engine made up of two different engines, one running on the waste heat of the other.

Existence of 'Thermodynamic Temperature'



The Thermodynamic Temperature Scale

- Composite engine made of two other engines, second uses ALL the waste heat of the first.
- No net heat enters reservoir at T_2, and so no reservoir is in fact required.



Composite engine has the same Q_1, Q_2 as the individual engines.
Defining f, some universal function, relating heat flow to temperature.
$\frac{Q_1}{Q_2} = f(T_1, T_2)$; $\frac{Q_2}{Q_3} = f(T_2, T_3)$.
While for the composite $\frac{Q_1}{Q_3} \; = \; f(T_1, T_3)$

$$\frac{Q_1}{Q_3} = \boxed{f(T_1, T_2).f(T_2, T_3) \; = \; f(T_1, T_3)}$$

The boxed expression can be satisfied iff f factorises, $f(T_1, T_2) = \frac{\theta(T_1)}{\theta(T_2)}$
Carnot engine efficiency provides 'natural' temperature scale, θ.
It is shown in the next lecture that $\theta \equiv T_{IG}$, i.e. $\theta(T_{IG}) = T_{IG}$.