- Review: Entropy and second law of thermodynamics
- Thermal engines and refrigerators

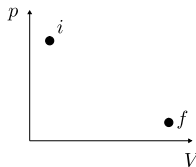For any thermodynamic system

Define the change of entropy:

$$dS = \frac{\delta Q}{T}$$

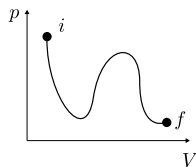for any infinitesimal reversible process.

For any *reversible* process:

$$\Delta S = S_{\text{final}} - S_{\text{initial}} = \int\limits_{\text{initial}}^{\text{final}} \frac{\delta Q}{T}$$

For an *irreversible* process:

CALCULATING THE CHANGE OF ENTROPY

A physics graduate drops a thin bottle with $100\,\text{g}$ of water at
$T_w = 80\,^{\circ}\text{C}$ into the ocean, which is at $T_o = 20\,^{\circ}\text{C}$, and waits for
the water to cool. Treating the water and ocean as an isolated
system, calculate

(I) the change of entropy of the water,

(II) the change of entropy of the ocean, and

(III) the net change of entropy of the ocean and water. Briefly
discuss whether this process is reversible or not.

(exam 2012-13)

CALCULATING THE CHANGE OF ENTROPY

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(I) the change of entropy of the water

Expect $\Delta S < 0$ since water releases heat.

$$\Delta S_{\text{water}} = \int\limits_{\text{initial}}^{\text{final}} \frac{\delta Q}{T} = \int_{T_w}^{T_o} \frac{c_w m_w dT}{T}$$

$$= c_w m_w \log \frac{T_o}{T_w}$$

If it's steam, not water: use the first law, $\delta Q = dU + p\, dV$

CALCULATING THE CHANGE OF ENTROPY

A physics graduate drops a thin bottle with $100\,\mathrm{g}$ of water at $80^\circ\mathrm{C}$ into the ocean, which is at $20^\circ\mathrm{C}$, and waits for the water to cool. Treating the water and ocean as an isolated system, calculate

(I) the change of entropy of the water

(II) the change of entropy of the ocean

$$
\begin{aligned}
\Delta S_{\mathrm{ocean}} &= \int\limits_{\mathrm{initial}}^{\mathrm{final}} \frac{\delta Q}{T} \qquad\qquad (T_{\mathrm{ocean}} = \mathrm{const})\\
&= \frac{1}{T_o} \int\limits_{\mathrm{initial}}^{\mathrm{final}} \delta Q\\
&= \frac{c_w m_w (T_w - T_o)}{T_o}
\end{aligned}
$$

A physics graduate drops a thin bottle with $100\,\mathrm{g}$ of water at $T_w = 80\,^\circ\mathrm{C}$ into the ocean, which is at $T_o = 20\,^\circ\mathrm{C}$, and waits for the water to cool. Treating the water and ocean as an isolated system, calculate

(I) the change of entropy of the water,

(II) the change of entropy of the ocean, and

(III) the net change of entropy of the ocean and water. Briefly discuss whether this process is reversible or not.

The net change of entropy $\Delta S = \Delta S_{\mathrm{ocean}} + \Delta S_{\mathrm{water}}$.

The process is clearly irreversible: the heat flows across the finite temperature difference.

The entropy of a *closed system* does not decrease with time.

$$\Delta S \geqslant 0 \qquad \text{(for a closed system)}$$

- *Closed* here means that we include *all* (sub)systems participating in the heat exchange
- for a reversible process $\Delta S = 0$

EXAMPLE: CHEMICAL REACTIONS

Chemical reactions can be *endothermic* (heat is necessary for and is absorbed during the reaction) or *exothermic* (heat is released during the reaction).

Chemists sometimes define *standard entropy* of a substance, S°: the value of entropy a mole of a substance has at $T = 298\,\text{K}$ and $p = 1\,\text{atm}$ [relative to $S(T = 0) = 0$].
In chemistry literature you can see something like this:

$$\Delta S^\circ_{\text{reaction}} = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$

This quantity can be either positive or negative without violating the second law of thermodynamics: chemical reagents do not form a closed system.
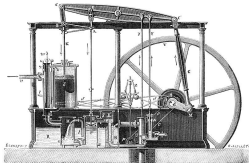
Heat engines

Watt steam engine, image from *La vapeur*,
A Guillemin, Paris, 1876

Heron's *Aeolipile* (1st century AD),
tikalon.com

diesel engine; image from
howstuffworks.com
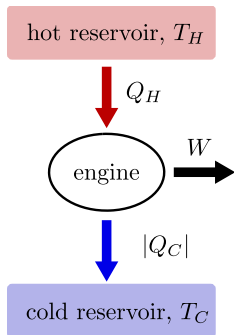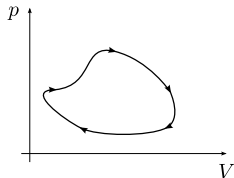

Siemens steam turbine (175 MW)

A heat engine operates using a *working fluid*, which undergoes a cyclic process.

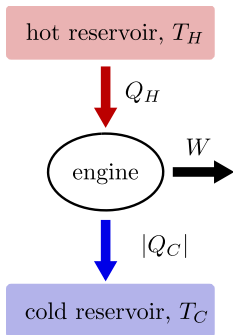$$\Delta U = 0 \qquad \Rightarrow \qquad Q_{\text{net}} = W_{\text{net}}$$

hot reservoir, T_H

Q_H

engine

W

$|Q_C|$

cold reservoir, T_C

- *Hot reservoir:* a heat source, transfers to the working fluid Q_H of heat per cycle
- *Cold reservoir:* absorbs rejected heat, Q_C per cycle

Sign convention: Q_H and Q_C are quantities of heat transferred *to* the working fluid:

$$Q_H > 0 \qquad Q_C < 0$$

HEAT ENGINES

hot reservoir, T_H

Q_H

engine

W

$|Q_C|$

cold reservoir, T_C

Net heat absorbed (by the engine), per cycle

$$Q_{\text{net}} = Q_H + Q_C = Q_H - |Q_C|$$

First law of thermodynamics:
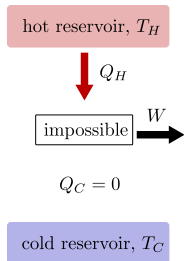
$$W = Q_{\text{net}} = Q_H - |Q_C|$$

NB: The heat rejected to a cold reservoir is gone for good.

Thermal efficiency of an engine:

$$e = \frac{\text{what we get}}{\text{what we pay for}}$$

$$= \frac{W}{Q_H} = 1 - \frac{|Q_C|}{Q_H}$$

hot reservoir, T_H

$\downarrow Q_H$

impossible $\xrightarrow{\ W\ }$

$Q_C = 0$

cold reservoir, T_C

Having a heat engine with $e = 100\%$ (that is, $Q_C = 0$) is impossible:

Second law of thermodynamics

It is impossible for any system to undergo a process in which it absorbs heat from a reservoir at a single temperature, and converts the heat *completely* into mechanical work, with the system ending up in the same state in which it began.

This is known as the "engine" formulation of the second law.

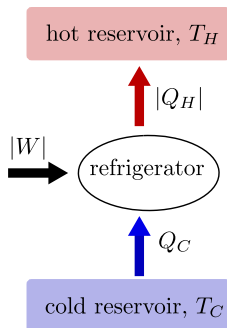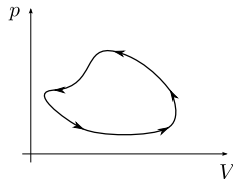Last lecture (a "refrigerator" formulation):

Second law of thermodynamics

It is impossible for any process to have *as its sole result* the transfer of heat from a cooler to a hotter body.

REFRIGERATORS

The cycle of the working fluid is run backwards, so that

$$W < 0$$
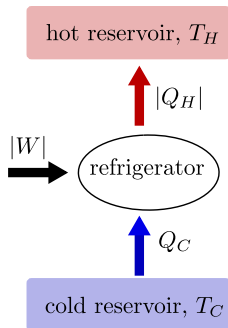

Each cycle, a refrigerator

- absorbs $Q_C > 0$ of heat from the cold reservoir
- and rejects $|Q_H|$ of heat to the hot reservoir ($Q_H < 0$)

Which requires a net *input* of work.

REFRIGERATORS

hot reservoir, T_H

$|Q_H|$

$|W|$

refrigerator

Q_C

cold reservoir, T_C

Net heat absorbed (by the refrigerator), per cycle

$$Q_{\text{net}} = Q_H + Q_C = Q_C - |Q_H|$$
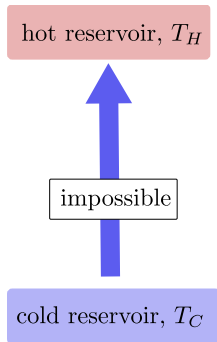
First law of thermodynamics:

$$|Q_H| = Q_C + |W|$$

A "good" refrigerator requires a minimum of mechanical work to remove maximum amount of heat from a cold reservoir.
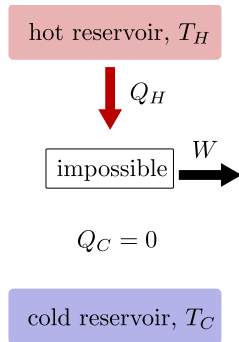*Coefficient of performance* of an refrigerator:

$$K = \frac{\text{what we get}}{\text{what we pay for}} = \frac{Q_C}{|W|} = \frac{Q_C}{|Q_H| - Q_C}$$

SECOND LAW OF THERMODYNAMICS

"Refrigerator" formulation:

hot reservoir, T_H

impossible

cold reservoir, T_C

"Engine" formulation:

hot reservoir, T_H

Q_H

impossible W

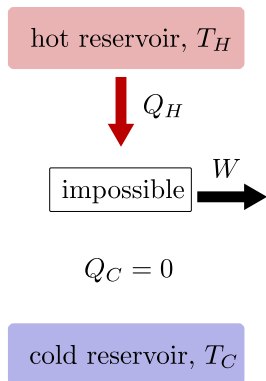$Q_C = 0$

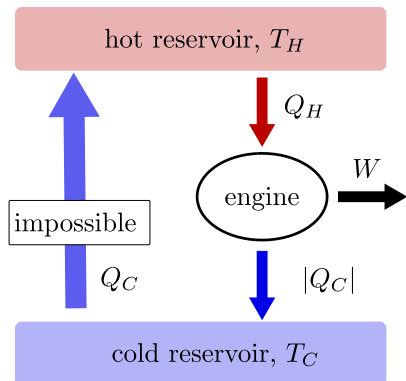cold reservoir, T_C

Closed system statement:

The entropy of a *closed system* does not decrease with time.

$$\Delta S \geqslant 0 \qquad \text{(for a closed system)}$$

SECOND LAW OF THERMODYNAMICS

All three formulations of the second law are equivalent.

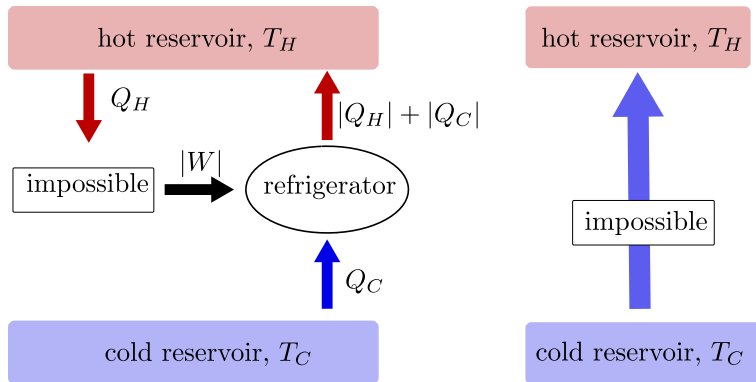Suppose we can violate the "fridge" formulation. Then:

...which violates the "engine" formulation.

SECOND LAW OF THERMODYNAMICS

All three formulations of the second law are equivalent.

Suppose we can violate the "engine" formulation. Then:

...which violates the "refrigerator" statement.