DTU

10060 Physics (Polyteknisk grundlag)

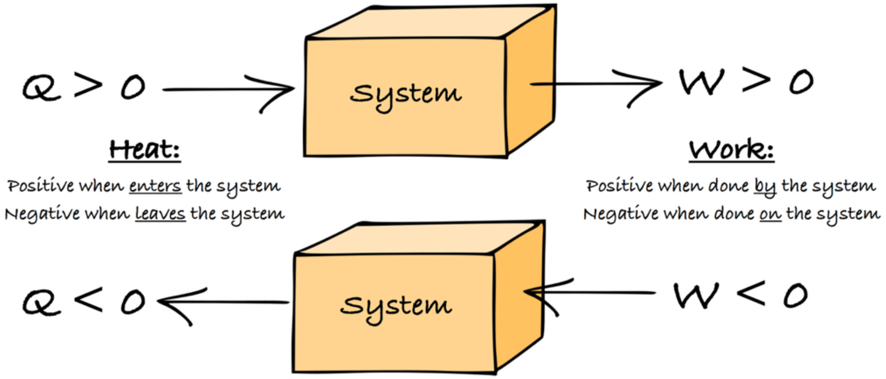
The Second Law of Thermodynamics

A word of caution

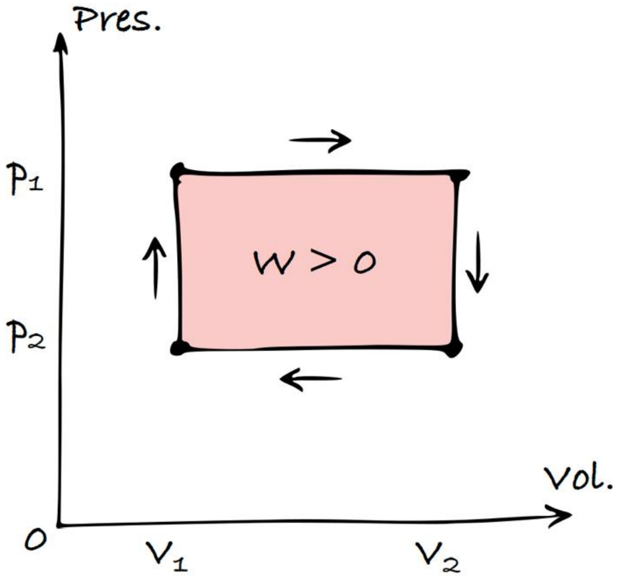
First law of Thermodynamics

$$\Delta E_{tot} = Q - W$$

… be mindful of the sign



… be careful with equating heat and work between different parts of the diagrams that look the same… they are usually different



Quizzes

Question	Average Grade	Standard Deviation
Question 1	69.23 %	46.15 %
Question 2	80.77 %	39.41 %
Question 3	69.23 %	46.15 %
Question 4	100 %	0.00 %
Question 5	76.92 %	42.13 %

Question 1

A gas is contained within a piston. Initially, the gas is at thermal equilibrium, with a pressure of 1 atm, volume of 2 L, and temperature of 300 K. If the gas is slowly compressed to a volume of 1 L while maintaining a constant temperature, which of the following best describes the work done and the heat transfer during this process?

- The system does work on the surroundings, and heat is absorbed by the system.
- The surroundings do work on the system, and heat is released by the system.
- The system does work on the surroundings, and heat is released by the system.
- The surroundings do work on the system, and heat is absorbed by the system.

Question 3

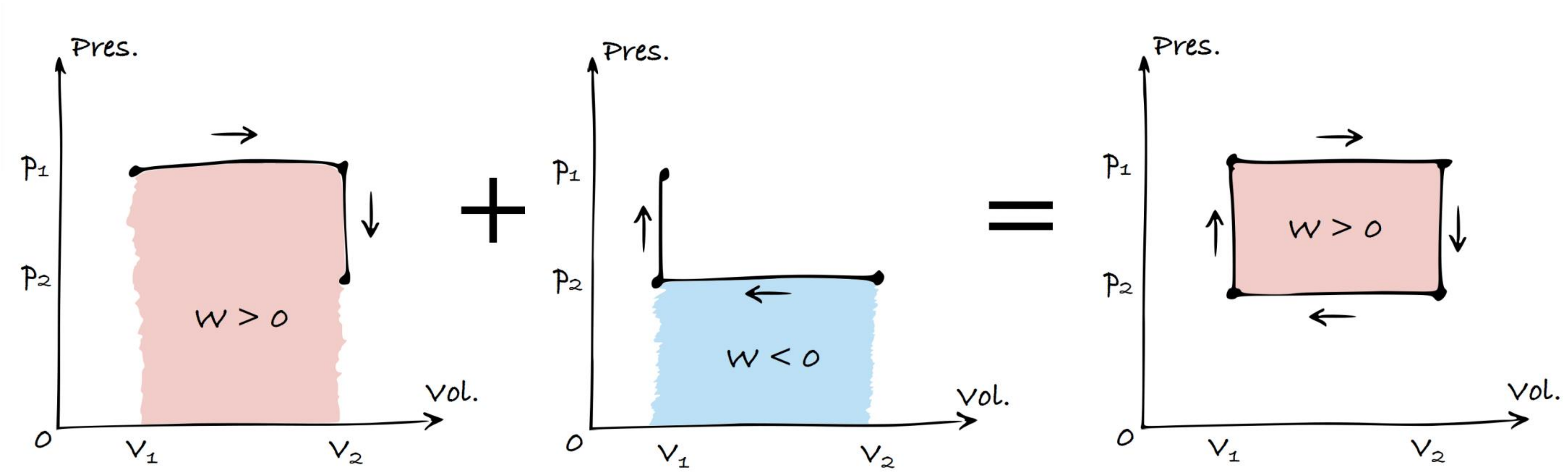
In a thermodynamic cycle an ideal gas undergoes two isothermal and two adiabatic processes. Starting from point A, the gas is compressed isothermally to point B, then compressed adiabatically to point C, expanded isothermally to point D, and finally expanded adiabatically back to point A. What is the net work done by the gas in this cycle?

- The net work done is positive along with a net internal energy gain.
- The net work done is negative along with a net internal energy loss.
- The net work done is positive and so is the heat.
- The net work done is positive and the heat is negative.

Reminder: Cyclic Transformation

In a cyclic transformation we get back to the original point

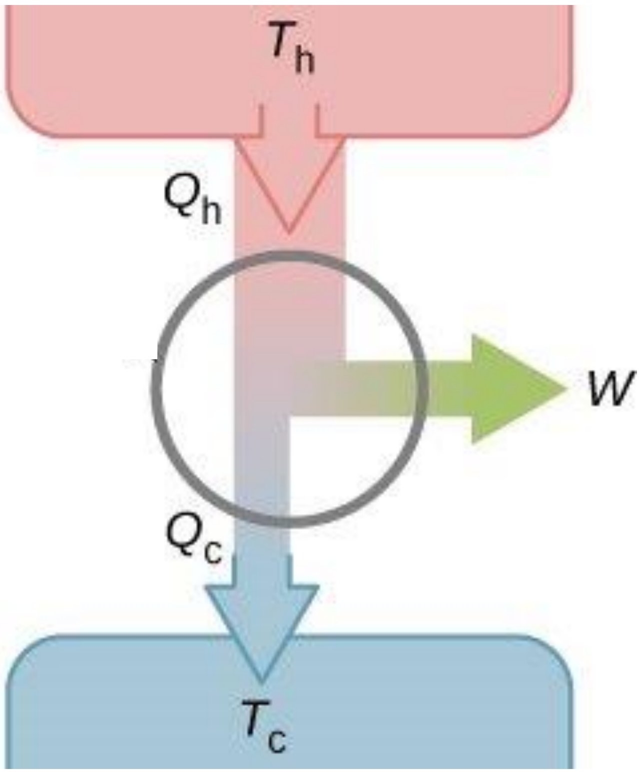
$$\Delta E_{tot} = 0 \quad \rightarrow \quad Q = W$$



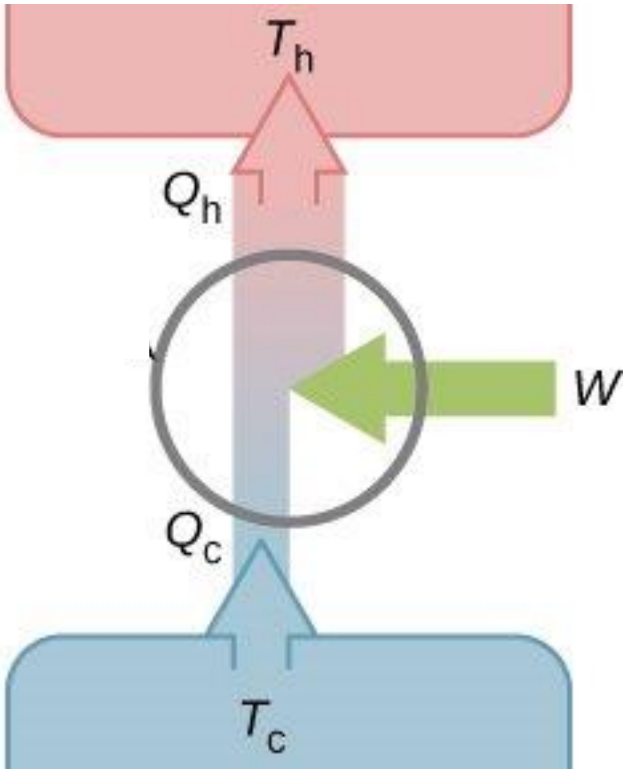
10060 Physics (Polyteknisk grundlag)

Statements of the 2nd law of thermodynamics

What are these?



Heat Engine



Heat pump / refrigerator

Efficiency of an engine

Efficiency is a measure of what we get out in relation to what we put in

Heat Engine

$$e = \frac{W}{Q_h}$$

Refrigerator

$$K_R = \frac{Q_c}{W}$$

Heat pump

$$K_P = \frac{Q_h}{W}$$

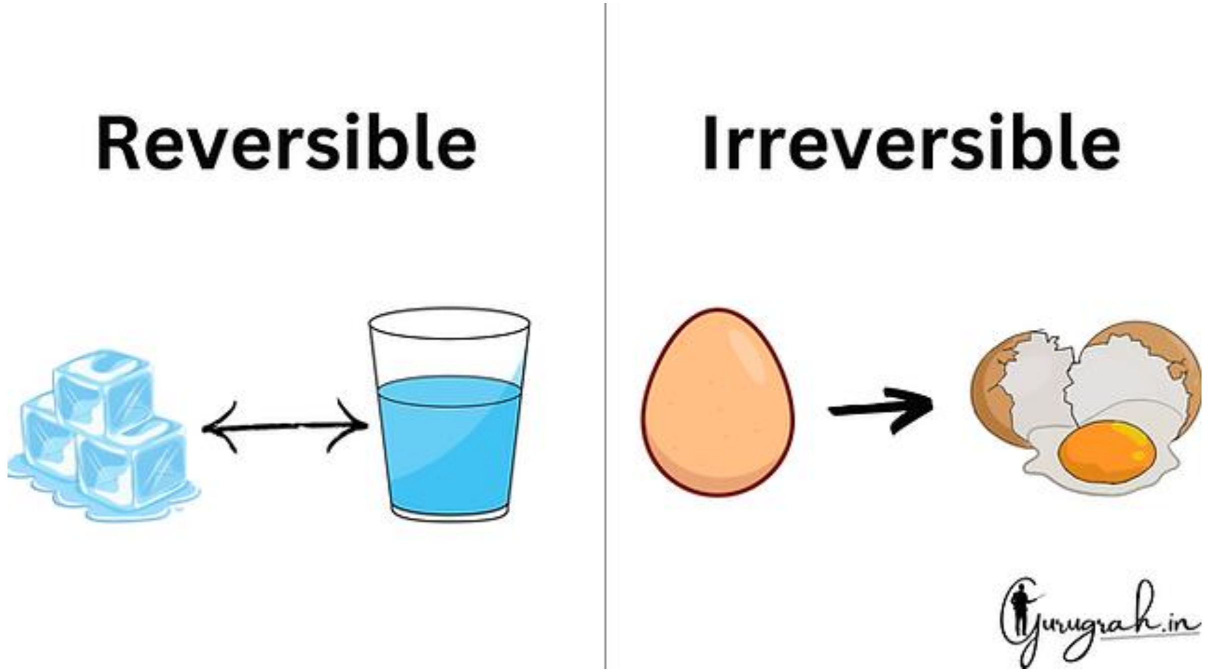
… but in a closed loop: $W = Q_h - Q_c$

$$e = 1 - \frac{Q_c}{Q_h}$$

$$K_R = \frac{Q_c}{Q_h - Q_c}$$

$$K_P = \frac{Q_h}{Q_h - Q_c}$$

Reversible and Irreversible processes



A **reversible process** is a process in which the system and environment can be restored to exactly the same initial stats they were in before the process occurred

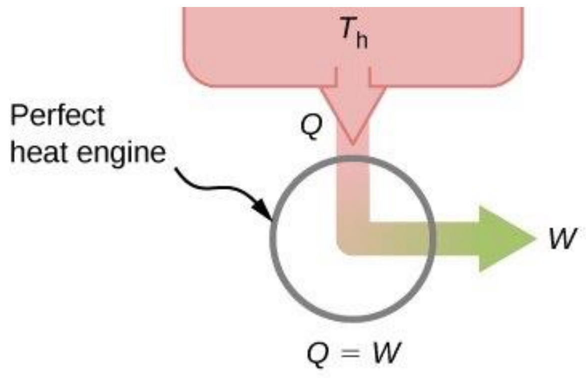
An **irreversible process** is a process in which the system and its environment cannot be restored to their original states at the same time

The hard part is often to restore the enviroment to its original state

First statement of 2nd law of thermodynamics

Kelvin's statement:

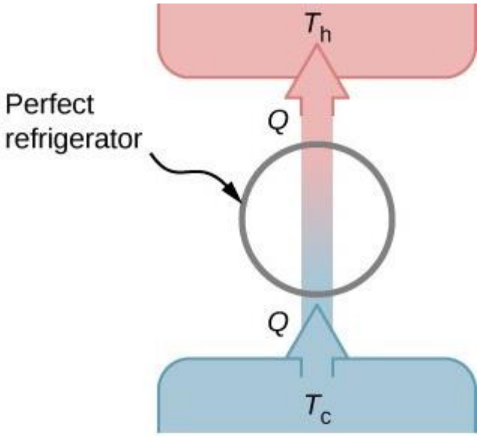
> It is impossible to convert the heat from a single source into work without any other effect



Second statement of 2nd law of thermodynamics

Clausius' statement:

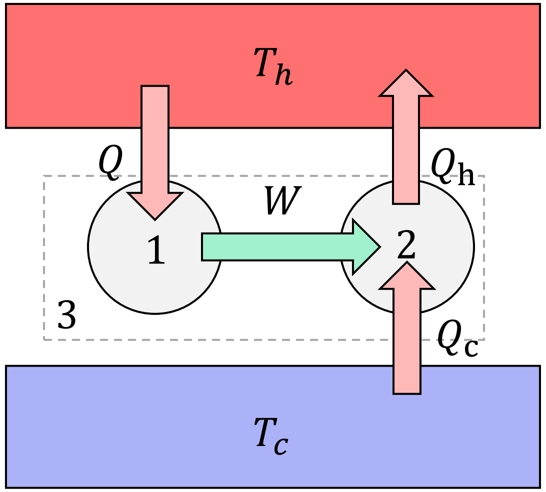
Heat never flows spontaneously from a colder object to a hotter object



Equivalence of the two statements

We do the proof by contraddiction:

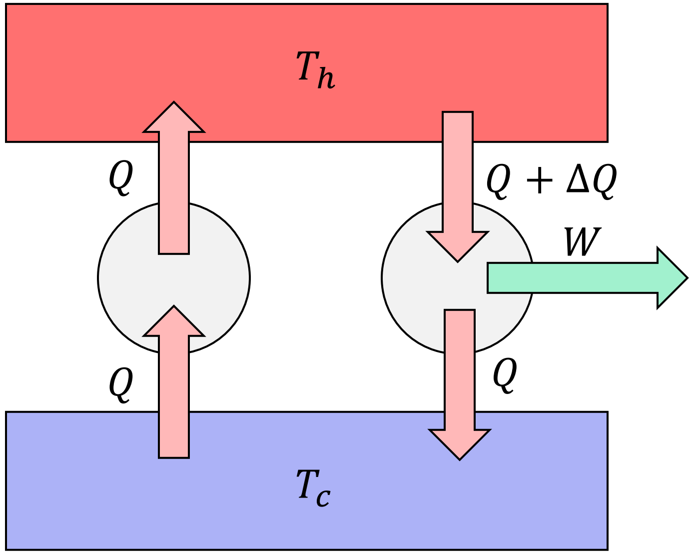
- Perfect heat engine exists



$$\begin{cases} Q = W & for\ 1 \\ Q_c - Q_h = W & for\ 2 \\ Q + Q_c = Q_h & for\ 3 \end{cases} \rightarrow \begin{cases} Q = Q_c - Q_h \\ Q = Q_h - Q_c \end{cases}$$

Heat from cold to hot

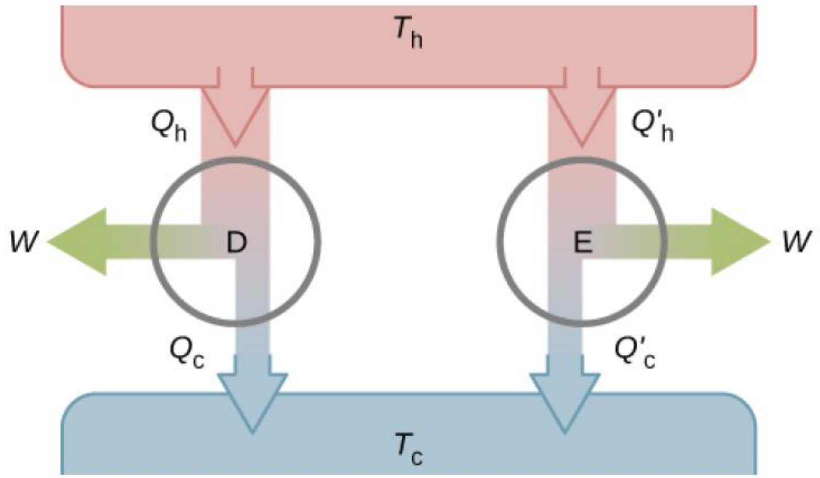
- Heat spontaneously goes from cold to hot



$$W = Q + \Delta Q - Q = \Delta Q \rightarrow W > 0$$

And no heat to cold reservoir

All reversible engines have the same efficiency



Assume: $e_E > e_D$

$$\frac{W}{Q'_h} > \frac{W}{Q_h} \rightarrow Q_h > Q'_h \rightarrow Q_c > Q'_c$$

$$Q_c - Q'_c > 0 \;\; and \; Q'_h - Q_h < 0$$

Heat from cold to hot

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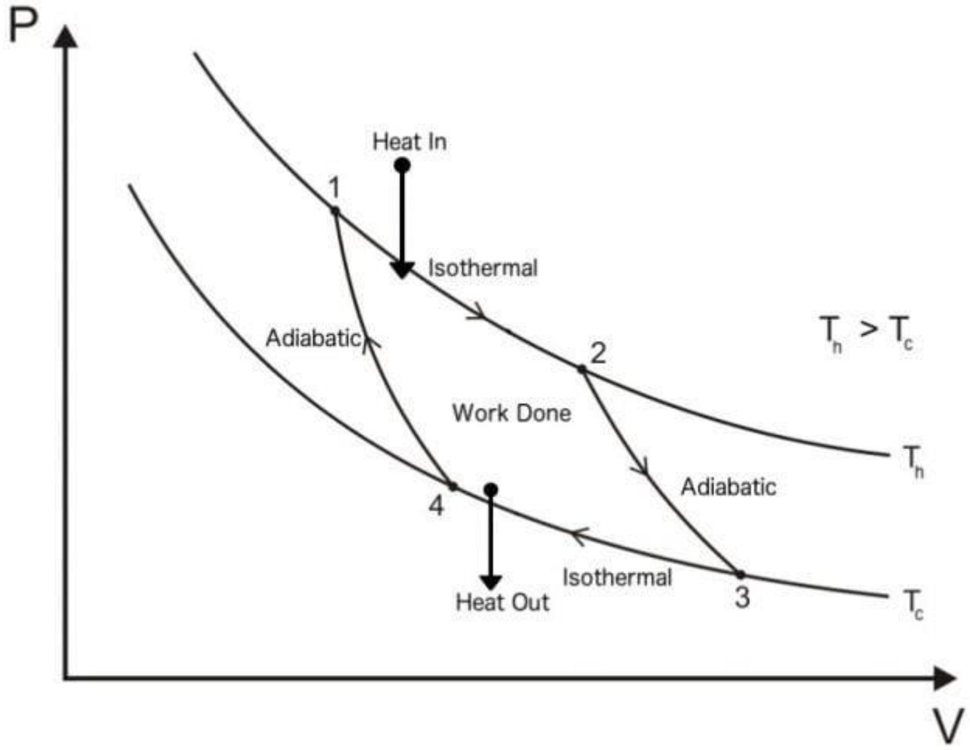
Engine cycles

The Carnot Heat Engine

N. Sadi Carnot
(1796-1832)

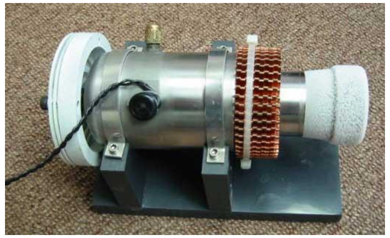
- The Carnot process is reversible (in principle)
- Rarely used, since it is not very practical

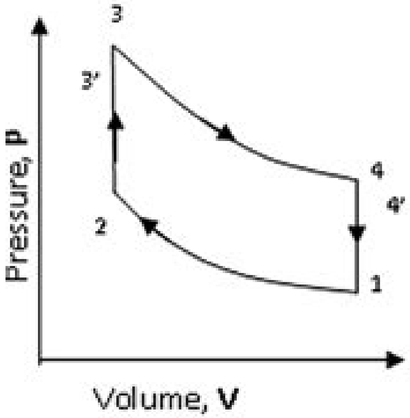


The Stirling Heat Engine

- More practical than the basic Carnot machine

cryo-cooler



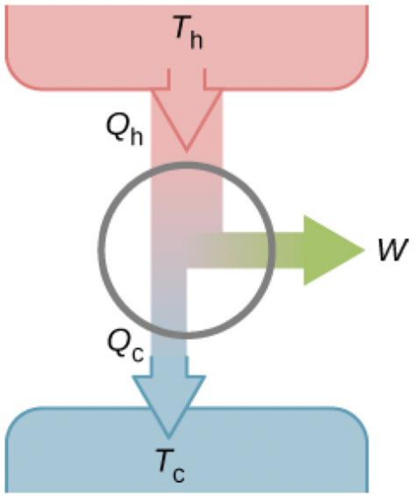


Robert Stirling

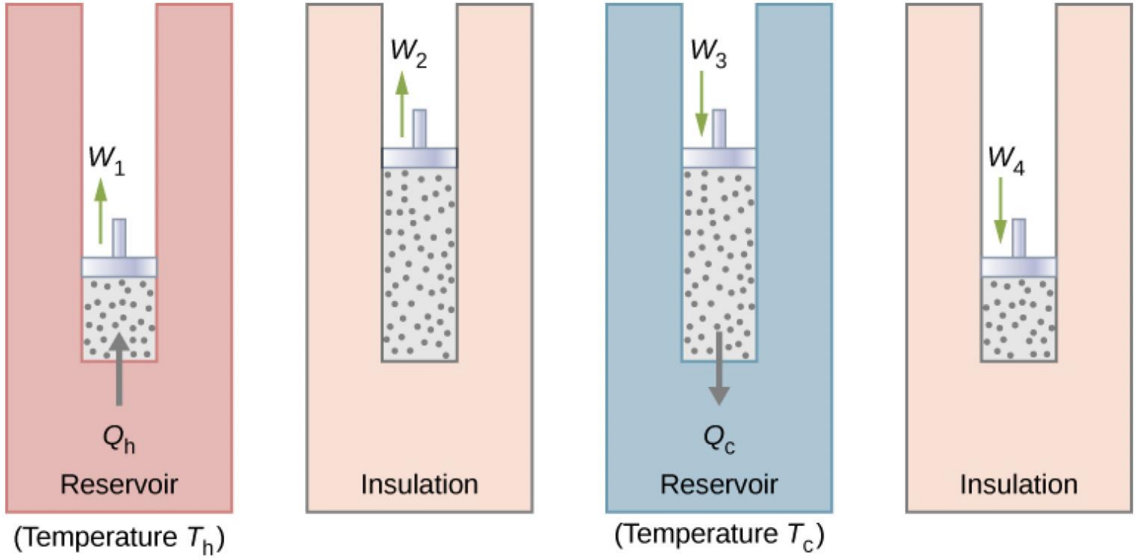
1790-1878

The Carnot Cycle

- Heat engine



- The separate phases



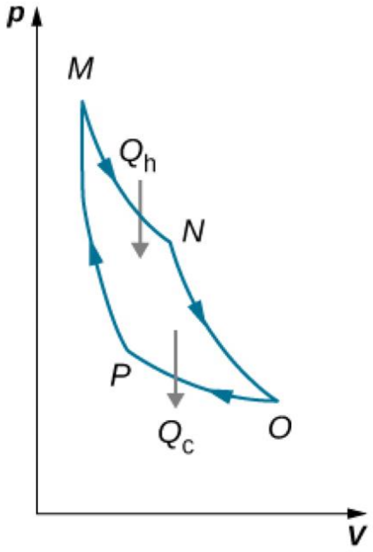
Step 1: Isothermal expansion ($M \rightarrow N$)

Step 2: Adiabatic expansion ($N \rightarrow O$)

Step 3: Isothermal compression ($O \rightarrow P$)

Step 4: Adiabatic compression ($P \rightarrow M$)

- PV diagram



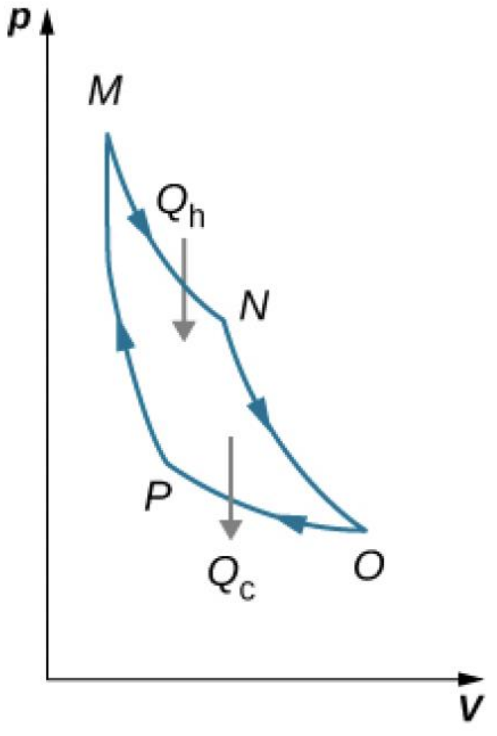
The efficiency of a Carnot Cycle using ideal gases

1. Isothermal expansion: $$Q_h = W_{MN} = nRT_h ln\frac{V_N}{V_M}$$

2. Adiabatic expansion: $$T_h V_N^{\gamma-1} = T_c V_O^{\gamma-1} \rightarrow \frac{V_N^{\gamma-1}}{V_O^{\gamma-1}} = \frac{T_c}{T_h}$$

3. Isothermal compression: $$Q_c = W_{OP} = nRT_c ln\frac{V_O}{V_P}$$

4. Adiabatic compression: $$T_c V_P^{\gamma-1} = T_h V_M^{\gamma-1} \rightarrow \frac{V_M^{\gamma-1}}{V_P^{\gamma-1}} = \frac{T_c}{T_h}$$



Efficiency:

$$e = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h}\frac{\ln(V_O/V_P)}{\ln(V_N/V_M)} \qquad since \ \frac{V_O}{V_P} = \frac{V_N}{V_M}$$

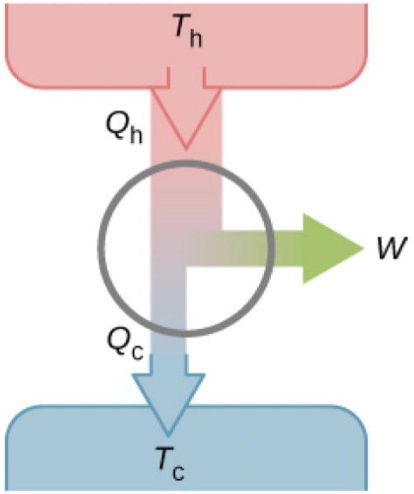
This result is universal!

$$e = 1 - \frac{T_c}{T_h}$$

Example: Let's optimize an Engine

A heat engine runs between a hot reservoir at T_h=500 K and a cold reservoir at T_c=300K. It absorbs Q_h=100 kJ from the hot side each cycle.

- What is the theoretical Maximum efficiency?
- A real engine can reach 70% efficiency of a Carnot engine, what's the Work output?
- Does the engine get more efficient if I cool T_c down by 100K or T_h up by 100K?



Baseline (500 K / 300 K):

$$\eta_C = 1 - \frac{300}{500} = 0.40 \rightarrow \eta_{\text{real}} = 0.70 \times 0.40 = 0.28 \rightarrow W = 0.28 \times 100 = 28\ \text{kJ}.$$

Option A: raise T_h to 600 K:

$$\eta_C = 1 - \frac{300}{600} = 0.50 \rightarrow \eta_{\text{real}} = 0.35 \rightarrow W = 35\ \text{kJ}.$$

Option B: lower T_c to 200 K:

$$\eta_C = 1 - \frac{200}{500} = 0.60 \rightarrow \eta_{\text{real}} = 0.42 \rightarrow W = 42\ \text{kJ}.$$

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Entropy

Definition of Entropy

Entropy is a thermodynamical state variable and is defined (for reversible processes) as:

$$\Delta S = \int_A^B \frac{dQ}{T}$$

Example: Melting ice

$$\Delta S = \frac{Q_f}{T_f} = \frac{mL_f}{T_f}$$

Example: Entropy Carnot Engine

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = \frac{Q_h}{T_h} - \frac{Q_c}{T_c} = 0$$

Entropy change in a reversible cycle is zero!

2nd law of thermodynamics in terms of entropy

For the entropy for a closed system and that of the universe it holds:

$$\Delta S \geq 0,$$

The entropy of the universe is defined as:

$$\Delta S_{universe} = \Delta S_{\mathrm{system}} + \Delta S_{\mathrm{environment}}$$

Example: Melting ice in a constant T>0 reservoir:

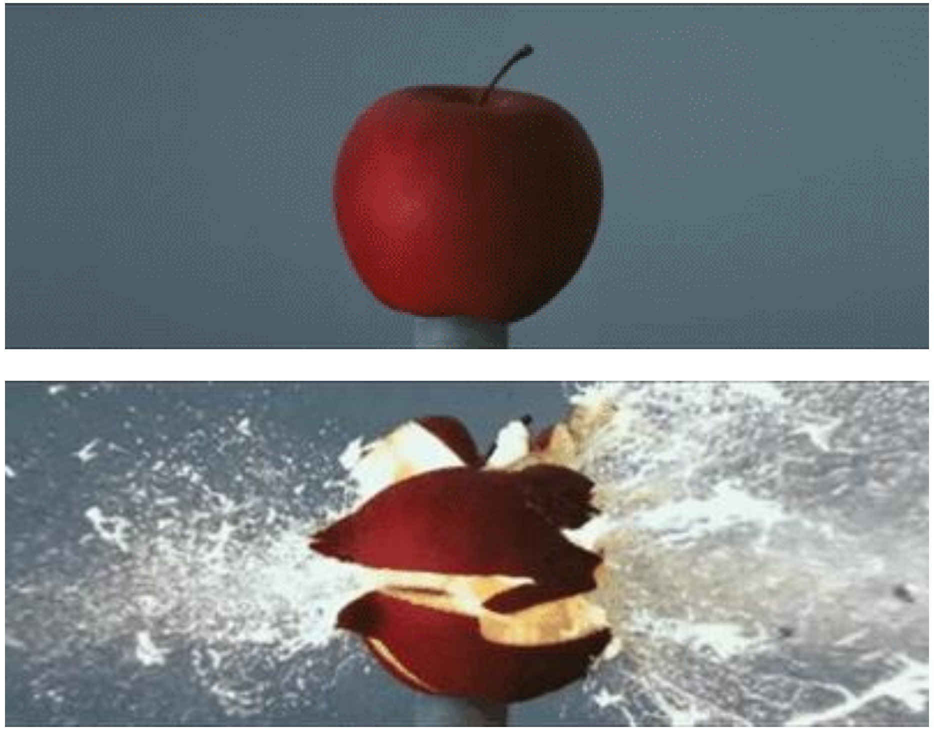
$$\Delta S_{universe} = \Delta S_{\mathrm{ice}} + \Delta S_{\mathrm{reservoir}} > 0$$

$$\Delta S_{\mathrm{ice}} = \frac{mL_f}{T_{ice}}$$

$$\Delta S_{\mathrm{reservoir}} = -\frac{mL_f}{T_{res}}$$

$$\Delta S_{universe} = mL_f \left(\frac{1}{T_{ice}} - \frac{1}{T_{res}} \right) > 0$$

The direction of increasing entropy is the direction of time



Hard to tell if played backwards

=> nearly reversible

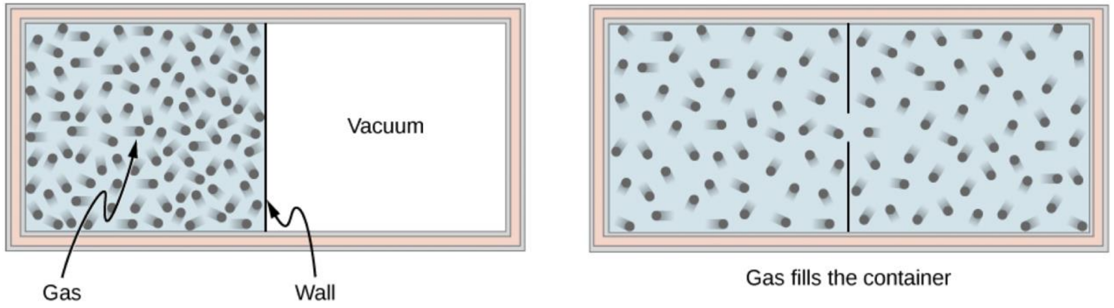
Obvious which way time goes forward
=> irreversible

Checkout Veritasium video on Entropy: https://www.youtube.com/watch?v=DxL2HoqLbyA

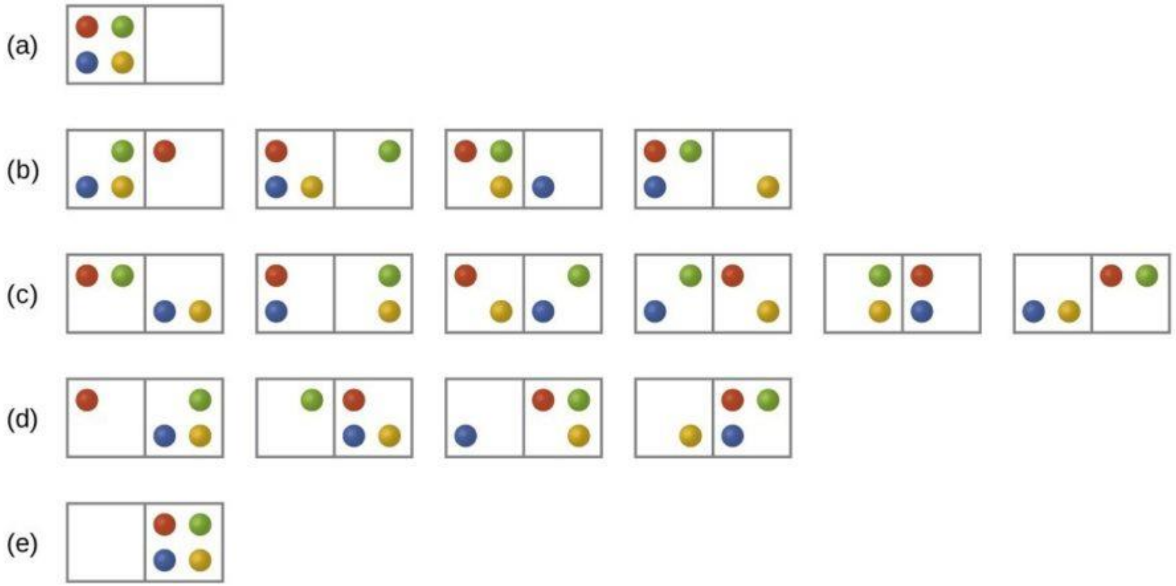
Entropy from a microscopic perspective

Entropy is a measure of disorder:

The more disorder the more entropy



Possible system microstates:



The macrostate with two and two particles is the most probable

2nd law of thermodynamics in terms of entropy

For the entropy for a closed system and that of the universe it holds:

$$\Delta S \geq 0,$$

3rd Law of Thermodynamics

The absolute zero temperature is not reachable - at least not with a finite number of cooling steps

$$\lim_{T \to 0} \Delta S = 0$$

… unfortunately you will need quantum mechanics to understand this statement