PHYS 10352

Part I: Classical Thermodynamics

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Week 3: The 2nd Law of Thermodynamics

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Recap

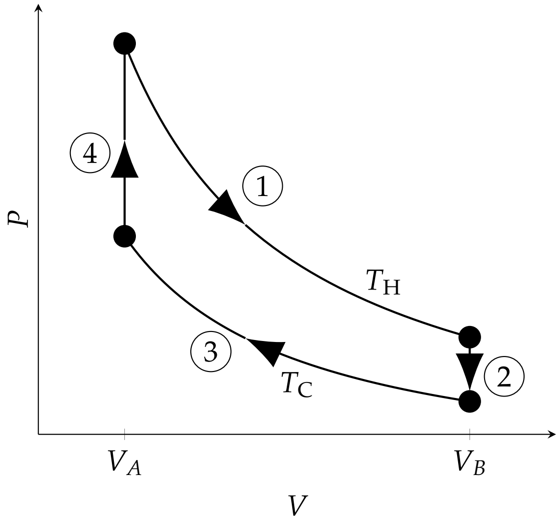
- The work done on a P–V system is given by $đW = -P\mathrm{d}V$.
- An **isothermal** process happens at *constant temperature* $\Rightarrow \Delta E = 0$ for an ideal gas.
- An **isobaric** process happens at *constant pressure*.
- An **isochoric** process happens at *constant volume* $\Rightarrow đW = 0$.
- An **adiabatic** process happens with *no heat flow* $\Rightarrow đQ = 0$.
- The **heat capacity** relates heat flow to temperature change: $đQ = C\,\mathrm{d}T$.
- Heat capacity is <u>different</u> for constant volume and constant pressure processes, and $C_P(T) > C_V(T)$.
- For an ideal gas: $C_P(T) = C_V(T) + nR$.
- Indicator diagrams allow us to visualise the changes resulting from different types of process.

Heat Engines

Heat engines are devices that produce work from heat. They operate in a cycle such that

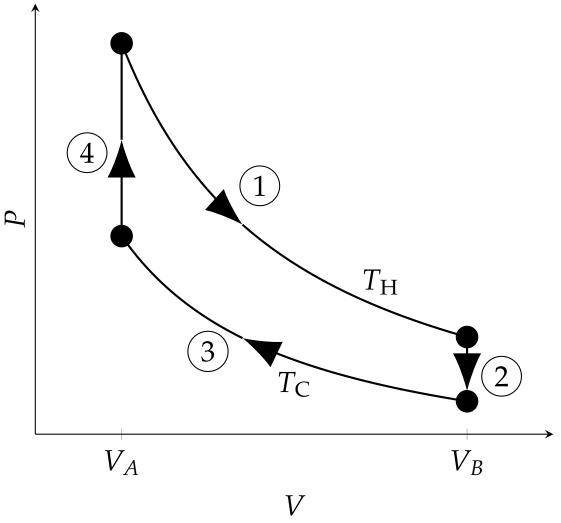
$$\Delta E = \oint dE = 0.$$

For example:



HEAT ENGINES

STIRLING CYCLE



(1) Isothermal expansion.
Work done by gas: $W_1 = nRT_H \ln\left(\frac{V_B}{V_A}\right)$
Heat absorbed: $Q_1 = W_1$

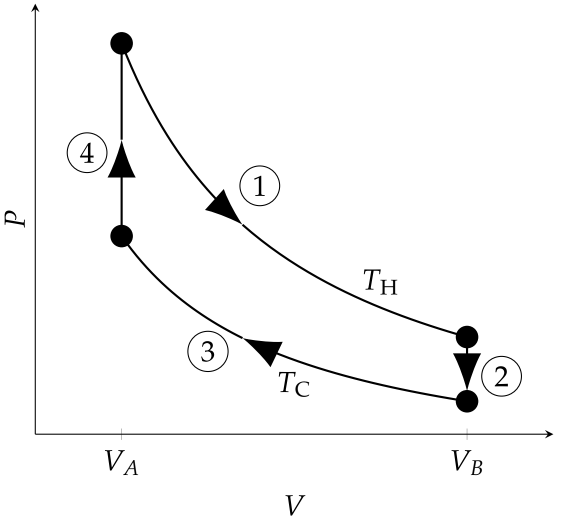
(2) Contact cooling
No work done.
Heat ejected: $Q_2 = E(T_H) - E(T_C)$

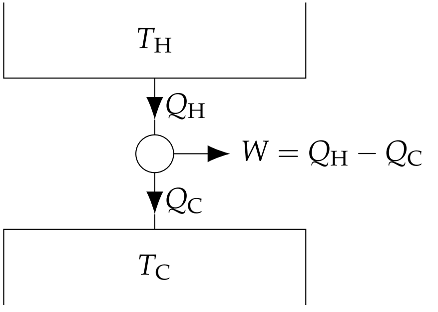
(3) Isothermal compression.
Work done on gas: $W_3 = nRT_C \ln\left(\frac{V_B}{V_A}\right)$
Heat ejected: $Q_3 = W_3$

(4) Contact heating
No work done.
Heat absorbed: $Q_4 = E(T_H) - E(T_C)$

Heat Engines

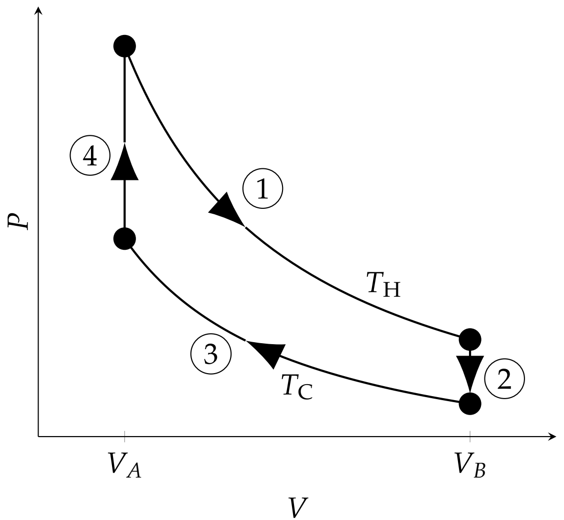
Stirling Cycle





Heat Engines

Stirling Cycle



The heat absorbed <u>from</u> the hot reservoir at T_H is

$$Q_H = Q_1 + Q_4$$

and the heat ejected <u>to</u> cold reservoir at T_C is

$$Q_C = Q_2 + Q_3.$$

From the 1st law we have, for the cycle,

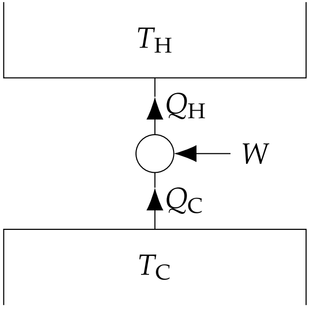
$$\Delta E = 0 = (-W) + (Q_H - Q_C).$$

Therefore,

$$W = Q_H - Q_C.$$

The *efficiency* of the engine is defined as:

$$\eta = \frac{\text{desired output}}{\text{required input}} = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} < 1.$$



We can also design a cycle that extracts heat, Q_C from a temperature reservoir in order to lower its temperature to T_C. To do this we need to put work into the system.

The "efficiency" of a refrigerator is

$$\eta_R = \frac{\text{desired output}}{\text{required input}} = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C}$$

Typically, $\eta_R > 1$, so it's a bit misleading to call it an efficiency. Often you will see it called the *coefficient of performance* (COP) instead.

The 2nd Law of Thermodynamics

...is difficult to express in a concise manner.

But it's basically about the direction in which heat flows (and entropy - but we'll get to that later).

- Systems at different temperatures reach equilibrium at an intermediate temperature. The reverse never happens.
- Heat naturally flows from hot bodies to cold bodies. For the reverse to occur, we require a refrigerator and a power supply.
- It is simple to use frictional work to warm a body, though it is far more difficult to produce work from heat; it requires an engine.

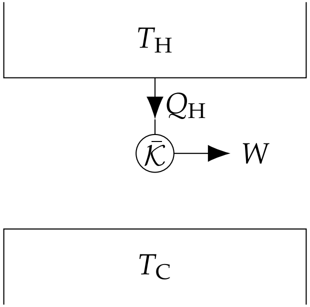
These statements also suggest a lack of symmetry between heat and work *even though they appear identically in the first law*: $\Delta E = W + Q$.

A recent, interesting (but quite long...) perspective from Stephen Wolfram: `https://writings.stephenwolfram.com/2023/01/how-did-we-get-here-the-tangled-history-of-the-second-law-of-thermodynamics/`

THE 2ND LAW OF THERMODYNAMICS

KELVIN-PLANCK STATEMENT

> *It is impossible to construct an engine which, operating in a cycle, produces no effect other than the extraction of heat from a reservoir and the performance of an equivalent amount of work.*

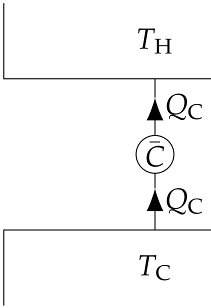


An engine $\bar{\mathcal{K}}$ that violates the Kelvin-Planck statement.

The 2nd Law of Thermodynamics

Clausius Statement

It is impossible to construct a refrigerator which, operating in a cycle, produces no effect other than the transfer of heat from a cooler body to a hotter one.



An engine $\bar{\mathcal{C}}$ that violates the Clausius statement.

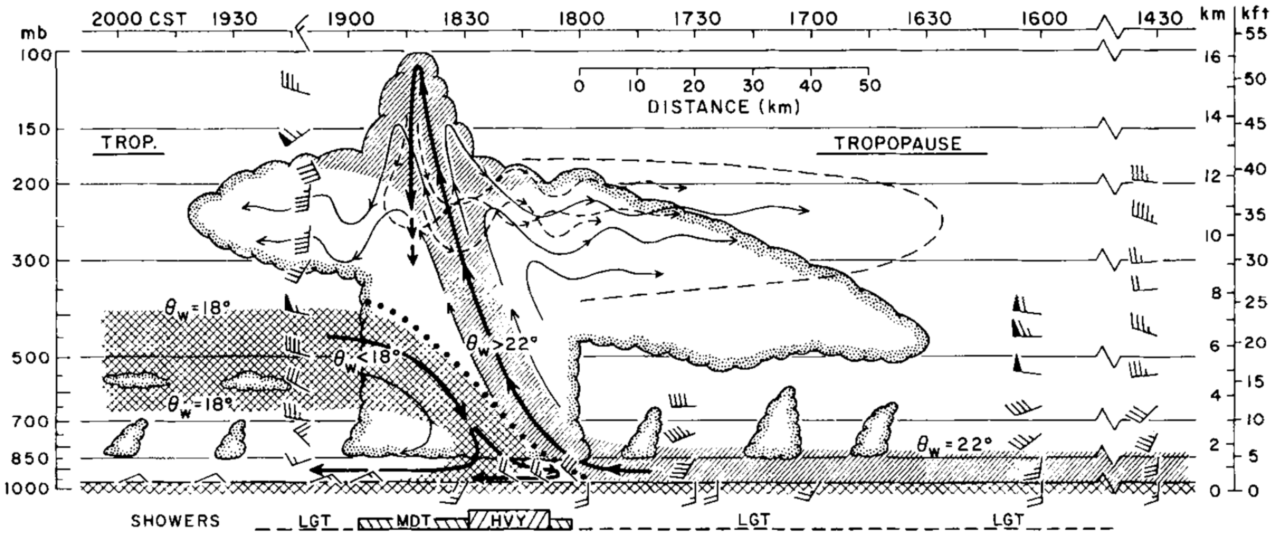
The Carnot Cycle

C'est à la chaleur que doivent être attribués les grands mouvements qui frappent nos regards sur la terre; c'est à elle que sont dues les agitations de l'atmosphère, l'ascension des nuages, la chute des pluies et des autres météores, les courants d'eau qui sillonnent la surface du globe et dont l'homme est parvenu à employer pour son usage une faible partie.[a]

– Sadi Carnot, 1824

[a] "It is to heat that we must attribute the great movements which influence our picture of the Earth; it causes the agitations of the atmosphere, the ascension of the clouds, the rain to fall and other weather, the currents of water that circle the surface of the globe and of which man makes use only a very meagre part."

THE CARNOT CYCLE



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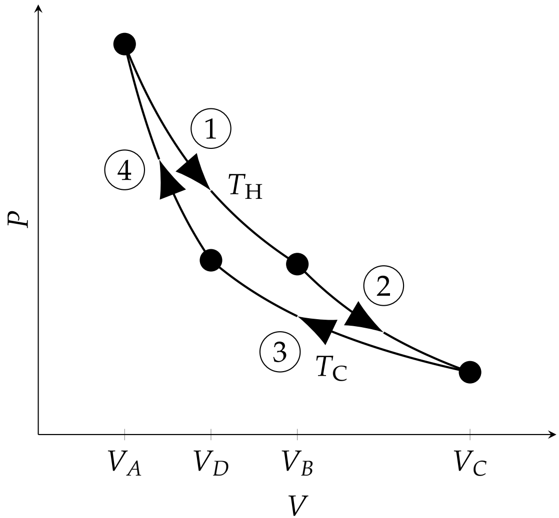
The Carnot Cycle



(1) Isothermal expansion at T_H, $\Delta E = 0$.

$$Q_H = \int_{V_A}^{V_B} \frac{nRT_H}{V} dV = nRT_H \ln \frac{V_B}{V_A}.$$

(2) Adiabatic expansion, $Q = 0$.

$$T_H V_B^{\gamma-1} = T_C V_C^{\gamma-1}$$

(3) Isothermal compression at T_C, $\Delta E = 0$.

$$Q_C = nRT_C \ln \frac{V_C}{V_D}.$$

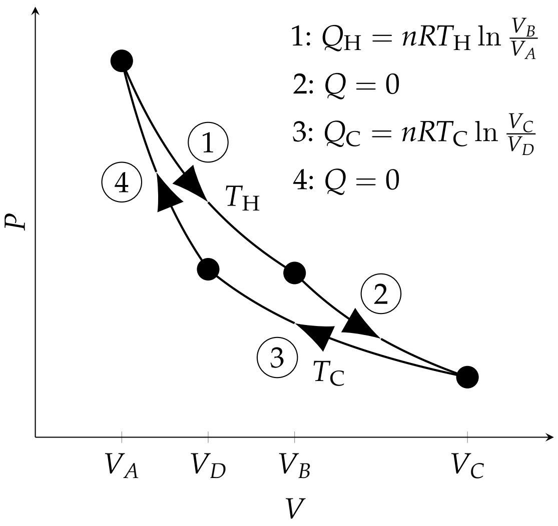
(4) Adiabatic compression, $Q = 0$.

$$T_H V_A^{\gamma-1} = T_C V_D^{\gamma-1}.$$

1. A reversible engine is the most efficient.
2. All reversible engines, operating between two heat baths, have the same efficiency, $\eta_{\mathcal{C}}$, depending only on T_H and T_C.

The Carnot Cycle

Carnot Efficiency



The efficiency is given by

$$\eta_{\mathcal{C}} = 1 - \frac{Q_{\mathrm{C}}}{Q_{\mathrm{H}}} = 1 - \frac{T_{\mathrm{C}}}{T_{\mathrm{H}}} \frac{\ln(V_C/V_D)}{\ln(V_B/V_A)}.$$

On the adiabats we know $TV^{\gamma-1} = \text{const.}$, so we can write:

$$T_{\mathrm{H}} V_B^{\gamma-1} = T_{\mathrm{C}} V_C^{\gamma-1};\ T_{\mathrm{H}} V_A^{\gamma-1} = T_{\mathrm{C}} V_D^{\gamma-1} \Rightarrow \frac{V_B}{V_A} = \frac{V_C}{V_D}.$$

This leaves us with a final form for the Carnot efficiency of:

$$\eta_{\mathcal{C}} = 1 - \frac{T_{\mathrm{C}}}{T_{\mathrm{H}}}.$$

This is valid for any reversible engine operating between two heat reservoirs with any working substance.

The Carnot Cycle

Worked Example - Heat Pump

It's a chilly day and the outside temperature is $-5°C$. Your house loses heat through its walls at a rate of 1 kW for each degree by which the inside temperature exceeds the outside temperature.

What is the maximum possible temperature inside your house if:

(a) you use 4 kW of electrical power to directly heat your house, or

(b) you use 4 kW of power to drive a heat pump?

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What is the maximum possible temperature inside your house if:

(a) you use 4 kW of electrical power to directly heat your house, or

(b) you use 4 kW of power to drive a heat pump?

The temperature inside the house will stop changing when the flow of heat *in* is equal to the flow of heat *out*, i.e. $\dot{Q}_{\text{in}} = \dot{Q}_{\text{out}}$.

In the case of direct heating, we have $\dot{Q}_{\text{in}} = 4 \times 10^3\,\text{W}$ and $\dot{Q}_{\text{out}} = 10^3\,\Delta T\,\text{W}$. If we equate these quantities then we find

$$\Delta T = \frac{4 \times 10^3}{10^3} = 4\,\text{K} \quad \Rightarrow \quad T_{\text{h}} = 268 + 4 = 272\,\text{K} = -1°\text{C}.$$

The Carnot Cycle

Worked Example - Heat Pump

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What is the maximum possible temperature inside your house if:

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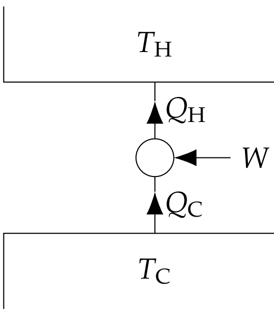
(b) **you use 4 kW of power to drive a heat pump**?

The temperature inside the house will stop changing when the flow of heat *in* is equal to the flow of heat *out*, i.e. $\dot{Q}_{\text{in}} = \dot{Q}_{\text{out}}$.



For a heat pump, the flow of heat into the house is given by the quantity Q_H. We also know that:

$$\eta = \frac{Q_H}{W} = \frac{T_H}{T_H - T_C} \quad \therefore \quad Q_H = \frac{W \cdot T_H}{T_H - T_C}.$$

Once again equating $\dot{Q}_{\text{in}} \equiv \dot{Q}_H$ and $\dot{Q}_{\text{out}}$, and knowing that $\dot{W} = 4 \times 10^3$ W, we can write:

$$\frac{W \cdot T_H}{T_H - T_C} = 10^3 (T_H - T_C) \quad \Rightarrow \quad T_H \simeq 303\,\text{K} = 30°\text{C}.$$

Summary

- Heat engines produce work from heat using a cycle where $\Delta E = \oint dE = 0$.
- The efficiency of an engine is defined as $\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} < 1$.
- The "efficiency" of a refrigerator is $\eta = \frac{Q_C}{W}$.
- The second law of thermodynamics can be expressed in multiple ways:
- the Kelvin-Planck formulation of the 2nd law says that it's impossible to convert heat to work perfectly;
- the Clausius formulation of the 2nd law says that it's impossible to construct a process which transfers heat from a colder to a hotter body without doing any work.
- Carnot's theorem: a reversible engine is the most efficient, and that all reversible engines operating between two heat baths have the same efficiency.
- The Carnot efficiency is given by:

$$\eta_C = 1 - \frac{T_C}{T_H}.$$