

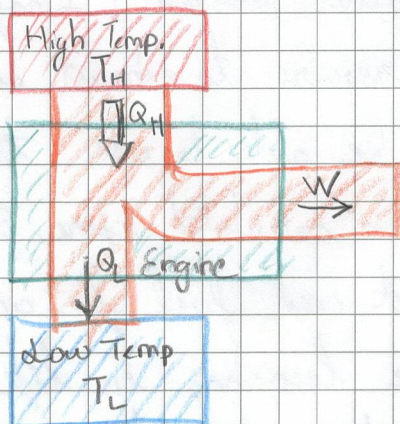
Second Law of Thermodynamics

The second law of thermodynamics is a physical law concerning heat and energy interconversions

Heat can flow spontaneously from a hot object to a cold object. Heat will not flow from a cold object to a hot object

Clausius statement of second law of thermodynamics

Heat engine is any device that converts thermal energy to work



Schematic diagram of energy transfers for a heat engine

Nota Bene! $Q_H > 0$ $Q_L > 0$ $W > 0$
a new notation!

We will be only interested in engines that repeat a cycle (returns back to initial state). This means $\Delta E_{int} = 0$ for the system at each cycle. A heat input Q_H at a high temperature T_H is partly transformed into work W and partly exhausted as heat Q_L at lower temperature. T_H and T_L are called the operating temperatures of the engine

most of our energy is generated by turbines
the material that is used turning the turbine
is working substance

Efficiency and the Second Law

Efficiency (e): (of a heat engine) the ratio of the work it does to the heat input

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

conservation of energy dictates

$$Q_H = W + Q_L$$

$$\rightarrow e = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

can a 100% efficient heat engine possible? Imagine it is. This would mean we would not require to exhaust anything in an engine. Then we would be able to use the energy stored in air (which we calculated before, it is very large) and we would not need fuel for anything. However, there are no free lunches in life, and we arrive at a second definition for the second law of thermodynamics

No device is possible whose sole effect is to transform a given amount of heat completely to work

Kelvin-Planck statement for 2nd law

Reversible and Irreversible Processes; the Carnot Engine

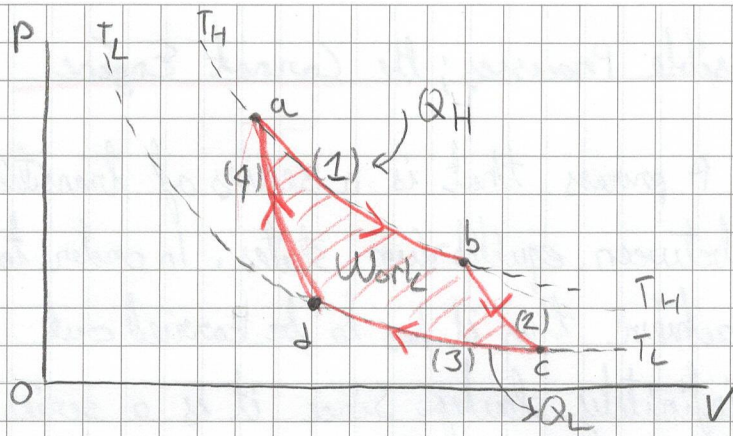
Reversible process: A process that is a series of transitions between equilibrium states. In order to achieve this it has to be carried out infinitely slowly. Since it is a series of transitions between equilibrium states the process can be traced back in reverse, and you end up with the same "path"

Irreversible process: All real processes are irreversible. There is friction, turbulence etc, that prevent system from being described as a series of transitions between equilibrium states. An irreversible process does not have a PV diagram

Reversible processes are important theoretically as it allows us to identify and study major trends in processes (and optimize them for engineering purposes)

Carnot's Engine

The Carnot engine makes use of a reversible cycle, by which we mean a series of reversible processes that take a given substance (the working substance) from an initial equilibrium state through many other equilibrium states and returns it again to the same initial state.



The Carnot cycle

The Carnot cycle begins at (a). (1) is isothermal expansion with a heat flow Q_H . At state (b) adiabatic expansion process (2) carries the state (c) at lower temperature T_L without any heat exchange. (3) is the compression of gas isothermally at T_L , which means Q_L will flow out from the system. Finally the gas is compressed adiabatically back to state (a) along (4)

The net work done in any reversible cycle engine is equal to the area enclosed by the cycle in PV diagram

The efficiency of a Carnot engine using an ideal gas:

$$e = 1 - \frac{Q_L}{Q_H}$$

$$W_{ab} = nRT_H \ln \frac{V_b}{V_a} \quad \text{(1) on path } a \rightarrow b$$

$$W_{ab} = Q_H \quad \text{for an isothermal process with ideal gas}$$

$$Q_H = nRT_H \ln \frac{V_b}{V_a}$$

Similarly

$$Q_L = nRT_L \ln \frac{V_c}{V_d}$$

The paths (2) and (4) ($b \rightarrow c$ and $d \rightarrow a$) are adiabatic

$$P_b V_b^\gamma = P_c V_c^\gamma$$

$$P_d V_d^\gamma = P_a V_a^\gamma$$

where $C_p/C_v = \gamma$. Using the ideal gas law

$$\frac{P_b V_b}{T_H} = \frac{P_c V_c}{T_L}$$

$$\frac{P_d V_d}{T_L} = \frac{P_a V_a}{T_H}$$

hence

$$T_H V_b^{\gamma-1} = T_L V_c^{\gamma-1}$$

$$T_L V_d^{\gamma-1} = T_H V_a^{\gamma-1}$$

or

$$\frac{V_b}{V_a} = \frac{V_c}{V_d}$$

Inserting this back

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H}$$

Hence the efficiency of a reversible Carnot engine can now be written:

$$\boxed{\epsilon_{\text{ideal}} = 1 - \frac{T_L}{T_H}}$$

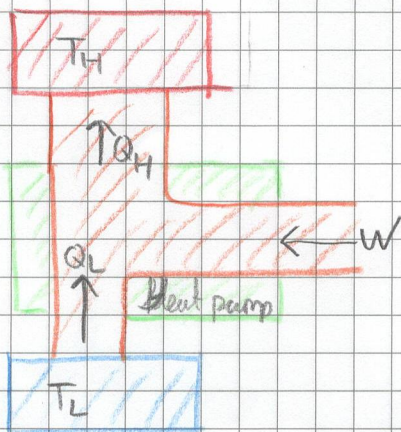
Carnot efficiency (Kelvin scale)

All reversible engines operating between the same two constant temperatures T_H and T_L have the same efficiency. Any irreversible engine operating between the same two fixed temperatures will have an efficiency less than this

This is known as the Carnot's theorem. It establishes the maximum efficiency of a real (irreversible) engine

O'K is not possible, this means no device is possible whose sole effect is to transform all heat to work

Heat pumps



You can do work on a working substance to make it pump heat from a colder temperature to hotter temperature. Depending on the scenario, a refrigerator, an air conditioner or a heat pump can be constructed

Heat pump

for a refrigerator or A/C coefficient of performance is

$$\text{COP} = \frac{Q_L}{W}$$

$$\text{COP}_{\text{ideal}} = \frac{T_L}{T_H - T_L}$$

for a heat pump used in heating a house

$$\text{COP} = \frac{Q_H}{W}$$

Entropy

It was not until the latter half of 19th century that the second law of thermodynamics was stated

in a general way microscopically in terms of entropy (S)

When dealing with entropy, the change is what matters not the absolute value

$$\Delta S = \frac{Q}{T}$$

Clausius statement for change in entropy due to heat added to the system

$$dS = \frac{dQ}{T}$$

In a reversible process from state a to b

$$\Delta S = S_b - S_a = \int_a^b dS = \int_a^b \frac{dQ}{T}$$

Showing Entropy is a state variable

Let's rewrite the result we had for Carnot cycle as

$$\frac{Q_H}{T_H} = \frac{Q_L}{T_L}$$

Note: to proceed, we need to go back to our initial relation where Q can be negative

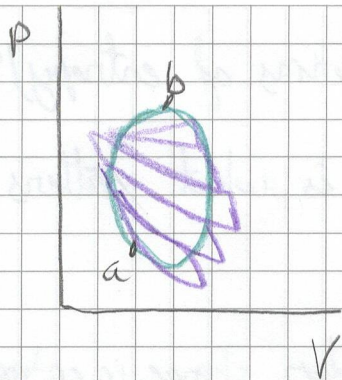
$Q > 0$ heat flows into the system, $Q < 0$ heat flows out the system

then

$$\frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0$$

For any reversible cycle, there is an approximation that is a combination of Carnot cycles. Hence we can generalise above

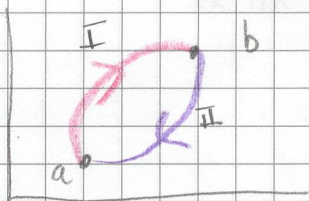
$$\oint \frac{dQ}{T} = 0$$



you can use Carnot cycles to paint any reversible cycle. More Carnot cycles mean better approximation. Note that each cycle's heat output Q_2 is negative of the Q_1 below it

$$\oint \frac{dQ}{T} = 0$$

Let's divide this cycle in two parts



$$\int_a^b \frac{dQ}{T} + \int_b^a \frac{dQ}{T} = 0$$

Since I is reverse of II

$$\int_a^b \frac{dQ}{T} = \int_a^b \frac{dQ}{T}$$

I II

If we set $dQ = dS$ this proves that the entropy of a and b is independent of path, so S is a state variable. Real processes are irreversible, however S is a state variable, and this allows us to determine ΔS in an irreversible process using a reversible process.

Entropy and the second law of Thermodynamics

S along with P, T, V, E_{int} and n are state variables. The flow of heat from the higher-temperature (T_H) object to the lower-temperature (T_L) object always results in an increase in the total entropy. The two objects eventually come to some intermediate temperature T_m . The heat lost by the hotter object ($Q_H = -Q$) is equal to the heat gained

by the colder one ($Q_L = Q$). Then total change in entropy is

$$\Delta S = \Delta S_H + \Delta S_L = -\frac{Q}{T_{HM}} + \frac{Q}{T_{LM}}$$

$\downarrow_{T_H \rightarrow T_M}$ $\downarrow_{T_L \rightarrow T_M}$

since hot object is always hotter than colder object throughout the process

$$\Delta S = Q \left(\frac{1}{T_{LM}} - \frac{1}{T_{HM}} \right) > 0$$

One object decreases in entropy, but the net change is positive

Entropy changes in a free expansion. Consider the adiabatic free expansion of n moles of an ideal gas from volume V_1 to volume V_2 where $V_2 > V_1$. Calculate the change in entropy (a) of the gas and (b) of the surrounding environment. (c) Evaluate ΔS for 1.00 mole, with $V_2 = 200V_1$.

Adiabatic free expansion
 $\downarrow Q=0$ $\downarrow W=0$

this is an irreversible process (the gas will not go back to V_1 spontaneously) so $\Delta S = \int_a^b \frac{dQ}{T}$ is not valid

$\rightarrow V$ (a state variable) is changing, while T (another state variable) stays constant. Is there a reversible process that satisfies the same criteria? Yes! Isothermal process!

$$dQ = dW = PdV$$

$$\Delta S_{\text{gas}} = \int \frac{dQ}{T} = \frac{1}{T} \int_{V_1}^{V_2} P dV$$

$$P = nRT/V$$

$$\Delta S_{\text{gas}} = \frac{nRT}{T} \int_{V_1}^{V_2} \frac{dV}{V} = nR \ln \frac{V_2}{V_1}$$

$\Delta S_{\text{gas}} > 0$ since $V_2 > V_1$

b) no heat transfer to the environment so $\Delta S_{\text{env}} = 0$
notice $\Delta S_{\text{gas}} + \Delta S_{\text{env}} > 0$

(c) $n=1.00$ $V_2=2.00V_1$ $\Delta S_{\text{gas}} = R \ln 2.00 = 5.76 \text{ J/K}$

Ex: Heat Transfer

A red-hot 2.00 kg piece of iron at temperature $T_1 = 880 \text{ K}$ is thrown into a huge lake whose temperature is $T_2 = 280 \text{ K}$. Assume the lake is so large that its temperature rise is insignificant. Determine the change in entropy (a) of the iron (b) of the lake

The process is irreversible, however there exists a state function we can use, specific heat. $Q = mc\Delta T$

where c is constant ($c = 450 \text{ J/kg}\cdot\text{K}$) then $dQ = mc dT$ becomes a quasistatic reversible process.

$$\begin{aligned} \Delta S_{\text{iron}} &= \int \frac{dQ}{T} = mc \int_{T_1}^{T_2} \frac{dT}{T} = mc \ln \frac{T_2}{T_1} \\ &= -mc \ln \frac{T_1}{T_2} \end{aligned}$$

$$\Delta S_{\text{iron}} = -(2.00 \text{ kg}) (450 \text{ J/kgK}) \ln \frac{880 \text{ K}}{280 \text{ K}} = -1030 \text{ J/K}$$

b) The initial and the final temperature of the lake is the same, $T = 280 \text{ K}$. The amount of heat received by the lake is:

$$Q = mc(T_2 - T_1) = (2.00 \text{ kg}) (450 \text{ J/kgK}) (880 \text{ K} - 280 \text{ K}) = 540 \text{ kJ}$$

this is actually an irreversible process locally, but the entropy change will be the same as the global reversible isothermal transfer of 540 kJ of heat at $T = 280 \text{ K}$

$$\Delta S_{\text{env}} = \frac{540 \text{ kJ}}{280 \text{ K}} = 1930 \text{ J/K}$$

Although the entropy of the iron rod decreases, the net change $\Delta S_{\text{env}} + \Delta S_{\text{rod}} = 900 \text{ J/K}$ is positive

Any reversible process can be considered as a series of quasistatic isothermal transfers of heat ΔQ between a system and the environment, which differ in temperature only by an infinitesimal amount, hence the change in entropy of the system and the environment is

$$\Delta S = \Delta S_{\text{sys}} + \Delta S_{\text{env}} = 0 \quad \text{any reversible process}$$

The entropy of an isolated system never decreases. It either stays constant (reversible process) or increases (irreversible process)

since all real processes are irreversible

The total entropy of any system plus that of its environment increases as a result of any natural process:

$$\Delta S = \Delta S_{\text{sys}} + \Delta S_{\text{env}} > 0$$

Second Law of Thermodynamics

Time's arrow: Entropy increase establishes a direction natural processes go. The natural direction how processes evolve is thus tied to entropy, and this is called time's arrow.

- Natural processes tend to move toward a state of greater disorder

- Even though the energy is conserved, in any natural process, some energy becomes unavailable to do useful work (it can be shown that the energy that becomes unavailable is equal to $T_L \Delta S$ where T_L is the lowest available temperature and ΔS is the total entropy increase). Eventually the universe is headed for heat death where no useful work is possible

Statistical Interpretation of Entropy and the Second Law

The ideas of entropy and disorder can be quantified. Statistics was used toward the end of 19th century by Ludwig Boltzmann for this problem.

We need two definitions to proceed

microstate: The position and speed of each particle

macrostate: Macroscopic properties of the system
(in terms of state variables like temperature etc.)

Microstates are usually not tractable discretely, but needs to be approached statistically. In general a number of microstates all correspond to the same macrostate

Ex: tossing of 100 coins

Macrostate	Number of microstates	Probability of macrostate
100H 0T	1	7.9×10^{-31}
90H 10T	1.7×10^{13}	1.4×10^{-17}
80H 20T	5.4×10^{20}	4.2×10^{-10}
60H 40T	1.4×10^{28}	0.01
55H 45T	6.1×10^{28}	0.05
50H 50T	1×10^{29}	0.08
45H 55T	6.1×10^{28}	0.05
40H 60T	1.4×10^{28}	0.01
20H 80T	5.4×10^{20}	4.2×10^{-10}
10H 90T	1.7×10^{13}	1.4×10^{-17}
0H 100T	1	7.9×10^{-31}

In this case, each microstate is equally probable. This is actually a very good approximation for many physically relevant systems. As you can see, highly "ordered" macrostates (such as all heads and all tails) are highly improbable, whereas highly disordered states (50 heads 50 tails) are much more probable. If you analyse the microstates of gas in terms of gas positions and speeds, you end up with a similar picture: Maxwell distribution

Boltzmann showed the entropy of a system in a given macrostate is

$$S = k_B \ln W$$

number of microstates

Boltzmann
constant

W is proportional to the probability of macrostate hence it is called thermodynamic probability or disorder parameter

Third law of thermodynamics

it is not possible to reach absolute zero in any finite number of process

(we shall see more details of this when we learn quantum principles a bit)