

OVERVIEW

- Arrow of time: reversible and irreversible processes
- Second law of thermodynamics
- Entropy (a thermodynamic view)

ARROW OF TIME

In mechanics (both classical and quantum) all elementary processes are time-reversible

In thermal physics, they are not:

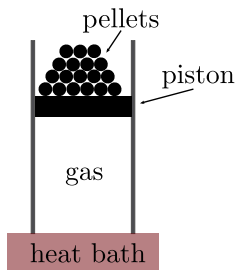
- *Dissipation*: Mechanical energy can be spontaneously converted to heat, but the reverse process does not happen spontaneously
- Heat flows from hotter bodies to colder ones, not the other way around

A related phenomenon: with time, degree of disorder tends to increase.

- Mechanical energy (kinetic energy of coordinated motion of molecules) is converted to heat (kinetic energy of random motion of molecules)
- Liquids mix, but never unmix spontaneously

REVERSIBLE AND IRREVERSIBLE PROCESSES

Recall from week 2:



The vessel is in contact with the heat bath, the temperature of the latter can be controlled externally. The piston is frictionless, and its mass can be controlled by adding/removing lead pellets.

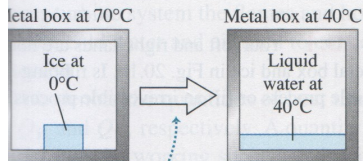
Add a few pellets, let the gas re-equilibrate, repeat \Rightarrow a *quasi-equilibrium* compression.

(Meaning: at every point in time the gas is approximately in a thermal equilibrium.)

quasi-equilibrium \Longleftrightarrow reversible

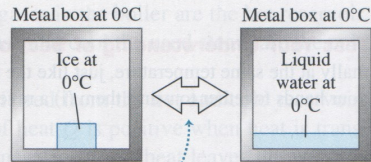
REVERSIBLE AND IRREVERSIBLE PROCESSES

(a) A block of ice melts *irreversibly* when we place it in a hot (70°C) metal box.



Heat flows from the box into the ice and water, never the reverse.

(b) A block of ice at 0°C can be melted *reversibly* if we put it in a 0°C metal box.



By infinitesimally raising or lowering the temperature of the box, we can make heat flow into the ice to melt it or make heat flow out of the water to refreeze it.

REVERSIBLE AND IRREVERSIBLE PROCESSES

Of course, all real processes are irreversible.

A reversible processes is an idealization, which is reasonable as long as $|\Delta p| \ll p$ and $|\Delta T| \ll T$ throughout: then we can view the whole process as a succession of equilibrium states.

If a process involves a finite temperature difference, it's definitely irreversible.

SECOND LAW OF THERMODYNAMICS

Common wisdom: Normally, heat flows from a hotter to a colder body.

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.

It is only one of several (equivalent) formulations.

NB: this combines thermodynamic quantities (temperature, heat), the arrow of time (heat *transfer*), and disorder (associated with heat)

ENTROPY

Consider an infinitesimal reversible isothermal expansion of the ideal gas:

$$V \rightarrow V + dV \quad \text{at} \quad T = \text{const}$$

From the first law of thermodynamics

$$\begin{aligned} \delta Q &= \delta W = p dV \quad (\text{using } pV = \nu RT) \\ &= \nu RT \frac{dV}{V} \end{aligned}$$

That is,

$$\frac{dV}{V} \propto \frac{\delta Q}{T}$$

dV/V can be viewed as a measure of the increase of disorder (in a larger volume there is more randomness for coordinates of molecules)

ENTROPY

For any system (not only ideal gas)



Define the change of entropy:

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

for any infinitesimal reversible process.

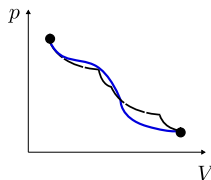
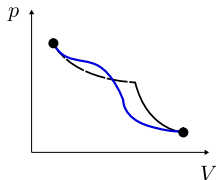
For any *reversible* process:

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

Units of S : Joules/Kelvin, J/K

ENTROPY

Q: What exactly do we mean by $\int_{\text{initial}}^{\text{final}} \frac{\delta Q}{T}$?



Use the fact that for an adiabatic process

$$\delta Q = 0 \quad \Rightarrow \quad dS = 0$$

and approximate any path by a sequence of adiabats and isotherms.

ENTROPY

For any *reversible* process:

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

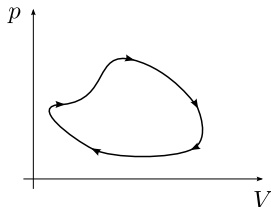
- Entropy is a *function of state* (cf pressure, temperature, or internal energy): it's a measure of disorder of a given thermodynamic state.
- We can only define the entropy difference (cf potential energy in mechanics). Conventionally, we fix

$$S(T = 0) = 0$$

ENTROPY

Q: What is the entropy change in a reversible cyclic process?

Since S is a function of state,

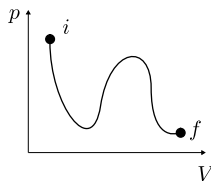
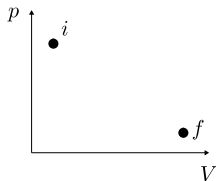


$$\begin{aligned}\Delta S &\equiv S_{\text{final}} - S_{\text{initial}} \\ &= \oint_{\text{initial}}^{\text{final}} \frac{\delta Q}{T} = 0\end{aligned}$$

for any reversible cyclic process.

ENTROPY

Q: What is the entropy change in an *irreversible* process?



Take any *reversible* process with the same initial and final states.

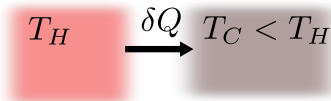
Since S is a function of state,

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

along the reversible path is the same as ΔS for an irreversible process.

ENTROPY

Consider two systems, at temperatures T_H and T_C , in thermal contact with each other.



Suppose that δQ of heat is transferred from a hot system to a colder one. What is the entropy change?

$$\Delta S_C = \frac{\delta Q}{T_C} > 0 \quad \text{cold system}$$

$$\Delta S_H = -\frac{\delta Q}{T_H} < 0 \quad \text{hot system}$$

$$\Delta S_{\text{net}} = -\frac{\delta Q}{T_H} + \frac{\delta Q}{T_C} > 0 \quad \text{net entropy change}$$

NB: finite temperature difference \Rightarrow the process is irreversible

SECOND LAW OF THERMODYNAMICS

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

$$\Delta S \geq 0 \quad (\text{for a closed system})$$

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

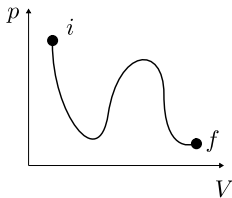
SECOND LAW OF THERMODYNAMICS

There seems to be a bit of a contradiction:

- On one hand, $\Delta S = 0$ for a reversible process.
- On the other hand, (three slides ago),

$$\Delta S = \int_{\text{initial}}^{\text{final}} \frac{\delta Q}{T} \neq 0$$

There is no contradiction.



This sketch only depicts a part of the closed system: somebody has to work to change state from i to f !