Reversibility

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.

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.

Processes in nature are always irreversible: far from equilibrium

Reversible process: idealized process infinitely close to thermodynamic equilibrium (quasi-equilibrium)

Necessary conditions for Reversibility

1. No work must be done by friction, viscous forces, or other dissipative forces that produce heat (no dissipation).
2. Heat conduction can only occur isothermally.
3. The process must be quasi-static so that the system is always in an equilibrium state (or infinitesimally close to one).
CPS question

An ideal gas is taken around the cycle shown in this $pV$–diagram, from $a$ to $b$ to $c$ and back to $a$. Process $b \rightarrow c$ is isothermal. Which of the processes in this cycle could be *reversible*?

- A. $a \rightarrow b$
- B. $b \rightarrow c$
- C. $c \rightarrow a$
- D. two or more of A., B., and C.
- E. none of A., B., or C.

Natural processes

Consider a free expansion:

Why is this process irreversible? Why the gas doesn’t compress itself to its original volume? (it wouldn’t violate the 1st law)

We have missed something…

We need another principle…
Heat engines

- Heat flows from the hot reservoir to the cold reservoir, producing work
- The process is cyclic

Work during a cycle:

\[ W = Q = Q_H + Q_C = |Q_H| - |Q_C| \]

We define thermal “efficiency” as

\[ e = \frac{W}{Q_H} = 1 + \frac{Q_C}{Q_H} = 1 - \frac{|Q_C|}{|Q_H|} \]

Refrigerators

- Mechanical work induces a heat flow from the cold reservoir to the hot reservoir
- The process is cyclic

Work during a cycle:

\[ -|W| = Q = Q_H + Q_C = |Q_C| - |Q_H| \]

We define the “coefficient of performance” as

\[ K = \frac{|Q_C|}{|W|} = \frac{|Q_C|}{|Q_H| - |Q_C|} \]
2nd 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 all the heat completely into mechanical work, with the system ending in the same state in which it began”

“engine”, or Kelvin-Planck statement

The second law “limits the availability” of energy and the ways in which it can be used and converted. We cannot have an engine with 100% efficiency: “No perpetuum mobile”

2nd 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 reservoir”

“refrigerator”, or Clausius statement
Reversible vs. Irreversible processes

To increase efficiency, we must avoid irreversible processes:

• When an engine absorbs or discards heat, it must be done at the temperature of the reservoirs $T_H$ or $T_C$, avoiding temperature drops (isothermal).

• When an engine performs work at some intermediate temperature $T$, it must avoid heat transfer (irreversible), therefore work at intermediate temperatures must be involve an *adiabatic* process.

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The Carnot cycle
(a reversible engine of maximum efficiency)

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The Carnot cycle

\[ Q_C = -\frac{T_C}{T_H} \ln \left( \frac{V_c}{V_d} \right) \]

We know that during the adiabatic processes:

\[ \frac{T_H V_b^{p-1}}{T_H V_a^{p-1}} = \frac{T_C V_c^{p-1}}{T_C V_d^{p-1}} \]

\[ \Rightarrow \frac{V_b}{V_a} = \frac{V_c}{V_d} \]

\[ \Rightarrow \frac{Q_C}{Q_H} = \frac{T_C}{T_H} \Rightarrow e_{\text{Carnot}} = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H} \]
The Carnot cycle and the 2\textsuperscript{nd} law

No engine can be more efficient than a Carnot engine operating between the same two temperatures

Entropy!

We define the differential increase in "entropy" $dS$ as:

$$dS = \frac{dQ_{\text{rev}}}{T}$$

Where the heat is added or removed in a reversible process

Note: This does not mean that the process has to be reversible for the entropy to change. This formula gives as a method for calculating the entropy change

As we shall see, entropy is a state function.
Entropy change for a Carnot cycle

The entropy change in the hot and cold reservoirs is:

\[ \Delta S_H = -\frac{|Q_H|}{T_H}; \Delta S_C = \frac{|Q_C|}{T_C} \]

We know that for a Carnot cycle:

\[ \frac{|Q_C|}{|Q_H|} = \frac{T_C}{T_H} \]

\[ \Rightarrow \Delta S_{Total} = -\frac{|Q_H|}{T_H} + \frac{|Q_C|}{T_C} = -\frac{|Q_H|}{T_H} + \frac{|Q_H| (T_C/T_H)}{T_C} = 0 \]

The entropy change during a reversible cycle is zero: the entropy change from a state 1 to a state 2 is independent of the path: S is a state function

Entropy of an ideal gas

For an ideal gas:

\[ dQ = dU + dW = dU + pdV \]

\[ dQ = C_v dT + nRT \frac{dV}{V} \]

This Eq. cannot be integrated unless we know how \( V \) depends on \( T \). This another way of saying that \( Q \) is not a state function.

However, if we divide by \( T \):

\[ \frac{dQ}{T} = C_v \frac{dT}{T} + nR \frac{dV}{V} = dS \]

If we assume that \( C_v \) remains constant, we can readily integrate it:

\[ \Delta S = \int \frac{dQ}{T} = C_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \]
Entropy changes for various processes

Isothermal expansion (T=constant):

\[ \Delta S = \int \frac{dQ}{T} = nR \ln \frac{V_2}{V_1} \]

The entropy change of the environment has the same magnitude but opposite sign:

In a reversible process, the entropy change of the “universe”=system+environment is zero.

Free expansion of an ideal gas:

Since entropy is a state function, it only depends on the initial and final state, and the change is the same for all processes, thus:

\[ \Delta S = \int \frac{dQ}{T} = nR \ln \frac{V_2}{V_1} \]

The entropy change of the environment is zero: The entropy of the universe is positive.

In an irreversible process, the entropy of the “universe increases.”
Entropy changes for various processes

Isobaric processes (P=constant):

$$\Delta S = \int \frac{dQ}{T} = \int C_p \frac{dT}{T} = C_p \ln \frac{T_2}{T_1}$$

This expression gives the entropy change of any process between the two temperatures, reversible or irreversible, as long as the pressure remains constant.

Entropy and the Second Law

No processes are possible in which the entropy of the universe decreases
Entropy and probability

Consider a free expansion:

Why is this process irreversible? Why the gas doesn’t compress itself to its original volume? (it wouldn’t violate the 1st law)

We can see that the \textit{probability} of finding \(N\) molecules in the smaller volume is

\[
p = \left( \frac{1}{2} \right)^N = \left( \frac{V_{\text{small}}}{V_{\text{large}}} \right)^N \quad \text{very small number!!!}
\]

\[
\ln p = N \ln \left( \frac{1}{2} \right) = N \ln \left( \frac{V_{\text{small}}}{V_{\text{large}}} \right) = nN_A \ln \left( \frac{V_{\text{small}}}{V_{\text{large}}} \right)
\]

We can compare this expression to the expression for the entropy change:

\[
\Delta S = \int \frac{dQ}{T} = nR \ln \frac{V_{\text{small}}}{V_{\text{large}}}
\]

\[
\Rightarrow \Delta S = \frac{R}{N_A} \ln p = k \ln p
\]

\text{\textcolor{red}{k: Boltzmann’s constant}}

Negative entropy fluctuations correspond to very low probability states. In an irreversible process, the universe moves from a state with low prob. to a state with high prob.