The Second Law of Thermodynamics

For irreversible processes in closed systems,

\[ \Delta S > 0 \]

For reversible processes in closed systems,

\[ \Delta S \geq 0 \]

2nd Law for any closed system \( \Delta S \geq 0 \)

Time has a direction
The Second Law and Carnot Engines

Perfect Refrigerator:

Perfect Engine X:
A mixture of 1.78kg of water and 262 g of ice at 0°C is, in a reversible process, brought to a final equilibrium state where the water/ice ratio is 1:1 by mass, still at 0°C.

a) Calculate the entropy change of the system during this process.

\[ m_{\text{tot}} = 2.042 \, \text{kg}, \quad \frac{1.780 \, \text{kg}}{1.021 \, \text{kg}} = 0.759 \, \text{kg freezes} \]

b) Now, the system is heated up with a bunsen burner and returned to its initial state. Find the entropy change during this irreversible process.

\[ Q = -mL_f = -0.759 \times (333.5 \, \text{kJ/kg}) = -253 \, \text{kJ} \]

\[ \Delta S = \frac{Q}{T} = \frac{-253 \, \text{kJ}}{273} = -927 \, \text{J/K} \leq \text{reversible} \]

b) Same \to +927 \, \text{J/K}
For the Carnot cycle shown, calculate the heat that enters and the work done on the system.

\[ \Delta S = \frac{Q}{T} , \quad Q = T \Delta S \]

**Top:** \[ Q_H = (400)(0.5) = 200 \text{ J} \]

**Bottom:** \[ Q = (250)(-0.5) = -125 \text{ J} \]

\[ Q_{\text{tot}} = 200 \text{ J} - 125 \text{ J} = 75 \text{ J} \]

\[ \eta = 1 - \frac{T_c}{T_H} = 1 - \frac{250}{400} = \frac{3}{8} = \frac{W}{Q_H} = \frac{W}{200} \implies W = 75 \text{ J} \]

First Law: \[ dQ + dW = \Delta E_{\text{int}} = 0 \text{ cycle} \]

\[ dQ = -dW , \quad -75 \text{ J} = W \]

\[ W_{\text{net}} \rightarrow \text{ work done on system} \]

\[ \text{Should be} < 0 \]
Some Questions:

• Heat energy flows from the sun to the earth. Show that the entropy of the Sun-Earth system increases during this process.

\[ \Delta S = \frac{-Q}{T_{\text{sun}}} \]

\[ \Delta S = \frac{Q}{T_{\text{earth}}} \]

\[ |\frac{Q}{T_{\text{earth}}}| > |\frac{Q}{T_{\text{sun}}}| \]

\[ \Delta S > 0 \]
Some Questions:

• Do living things violate the Second Law of Thermodynamics? As a chicken grows, for example, it becomes more and more ordered and organized, decreasing its own entropy. How do we reconcile this with the Second Law?

\[ |\Delta S_{\text{chicken feed}}| > |\Delta S_{\text{chicken}}| \]
Some Questions:

• Can one use terrestrial thermodynamics, which is known to apply to bounded and isolated bodies, for the whole universe? If so, is the universe bounded, and from what is it isolated?
Entropy and Probability

\[ W = \frac{8!}{5! \cdot 3!} \]

Configuration \rightarrow how many \( \mu \)-states

\[ W = \frac{N!}{N_L! \cdot (N-N_L)!} \]

8 atoms:

\[ \frac{P(4,4)}{P(8,0)} = \frac{70}{1} \leq 70 \times more \ probable \]

50 atoms:

\[ \frac{P(25,25)}{P(50,0)} = 1.2 \times 10^{14} \]

\[ S = k_B \ln W \]
Consider a container that is divided in two sections. Initially, \( N \) molecules are in one section, and the other side is empty. Compute the multiplicity and the entropy of this state. After a hole is punched in the partition, the gas fills the entire container uniformly. The most probable state has \( N/2 \) molecules on either side. Find the multiplicity of the final state. What is the change in entropy for the free-expansion process?

\[
\ln N! = N \ln N - N \quad \text{(Stirling's Formula)}
\]

a) \( \log w = 1 \rightarrow \text{one way,} \quad S = k \log w = k \log(1) = 0 \)

b) \( w = \frac{N!}{(N/2)! (N/2)!} = \left[ \frac{N!}{(N/2)!} \right]^2, \quad S = k \ln N! - 2k \ln \left( \frac{N!}{2!} \right) \rightarrow \text{Stirling} \)

\[
S = kN \ln N - kN - 2k \frac{N}{2} \ln \frac{N}{2} + 2k \frac{N}{2} = kN \ln N - kN \ln \frac{N}{2}
\]

\[
= kN \ln N - kN \ln N + kN \ln 2 = kN \ln 2 = nR \ln 2
\]

\((\text{same answer as before})\)
Boltzmann Distribution

System

\[ U_0 = \text{total } E \]

Reservoir R

\[ U_0 - \varepsilon_s \]

System \( S, \varepsilon_s \)

System in thermal eq. w/ Reservoir

\[ U_0 \gg \varepsilon_s \]

define:

# States in Reservoir \( w(U_0 - \varepsilon_s) \)

\[ S = k_B \ln w, \ e^{S/k_B} = w \]

Probabilities:

\[
\frac{\text{Prob}(\varepsilon_1)}{\text{Prob}(\varepsilon_2)} = \frac{w(U_0 - \varepsilon_1)}{w(U_0 - \varepsilon_2)} = \frac{e^{\frac{1}{k_B} S(U_0 - \varepsilon_1)}}{e^{\frac{1}{k_B} S(U_0 - \varepsilon_2)}}
\]

\[ = e^{\frac{1}{k_B} [S(U_0 - \varepsilon_1) - S(U_0 - \varepsilon_2)]} = e^{\frac{\Delta S}{k_B}} \]

where \( \Delta S = S(U_0 - \varepsilon_1) - S(U_0 - \varepsilon_2) \)

Taylor series:

\[ S(U_0 - \varepsilon_1) \approx S(U_0) - \varepsilon_1 \frac{\partial S}{\partial U} + \cdots \]

\[ \equiv S(U_0) - \varepsilon_1 / T \]

\[ \Delta S = S(U_0) - \varepsilon_1 / T - (S(U_0) - \varepsilon_2 / T) = - \frac{(\varepsilon_1 - \varepsilon_2)}{T} \]

If \( dW = 0 \)

\[ dQ = dE = dU \]

\[ \frac{\partial S}{\partial U} = \frac{\partial S}{\partial Q} = \frac{1}{T} \]
\[
\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = e^{-\frac{(\varepsilon_1 - \varepsilon_2)}{k_B T}} = \frac{e^{-\varepsilon_1/k_B T}}{e^{-\varepsilon_2/k_B T}} \quad \text{Boltzmann factor}
\]

\[
P(\varepsilon) \propto e^{-\varepsilon/k_B T}, \quad P(\varepsilon) = \frac{e^{-\varepsilon/k_B T}}{Z}
\]

\[
Z = \sum_s e^{-\varepsilon_s/k_B T} \quad \text{total probability} \quad \text{(Partition Function)}
\]

no dependence on \( N \), size of system \( \rightarrow \) just \( \varepsilon_s, T \).
A 12.6g ice cube at -10.0°C is placed in a lake whose temperature is 15.0°C. Calculate the change in entropy of the system as the ice cube comes into thermal equilibrium with the lake.

\[ \Delta S_{\text{Lake}} = -\frac{Q_{\text{ice}}}{T_{\text{Lake}} < \text{const.}} = -\frac{-5270}{288} = -18.29 \text{ J/K} \]

\[ Q_{\text{ice}} = m c_I (10 K) + mL_f + mc_w(15K) = 5270 \text{ J} \]

\[ dS = \frac{dQ}{T}, \quad \Delta S_{\text{ice}} = mc_I \ln \left( \frac{273}{263} \right) + \frac{mL_f}{273} + mc_w \ln \left( \frac{288}{273} \right) \]

\[ = 19.24 \text{ J/K} \]

\[ \Delta S_{\text{total}} = -18.29 + 19.24 = 0.95 \text{ J/K} > 0 \]