Example 20.6

1.00kg of water at 0°C is slowly (quasi-statically) heated to 100°C. (no phase change) Calculate $\Delta S$.

From each of the infinitesimal step, we have $dS = \frac{dQ}{T}$

$$
\Delta S = \int_{T_i}^{T_f} \frac{dQ}{T} = \int_{T_i}^{T_f} \frac{mc_w dT}{T} \\
= mc_w \ln \left( \frac{T_f}{T_i} \right) \\
= 1.00kg \left( \frac{4190J}{kg \cdot K} \right) \ln \left( \frac{100 + 273}{0 + 273} \right) \\
= 4190J / K \left( 0.3121 \right) = +1308J / K > 0
$$

(Entropy increases as water get hotter and water molecules get more agitated.)
Example of an Irreversible Mixing Process

Heat exchange between two objects at different temperatures

Hot iron (at $T_h$) $\rightarrow$ water bath (at $T_c$)

(MAKE IT SIMPLE: assume the heat from the hot iron is just hot enough to warm the water but not boiling any off $\rightarrow$ reaching $T_c < T_{final} < T_h$)

As soon as they are in thermal contact, heat $Q$ will spontaneously flow between them until they reach thermal equilibrium.

This process CANNOT be done quasi-statically!
Example of an Irreversible Mixing Process

However, individually, an infinitesimal $dQ$ (in and out) of the individual objects can be calculated as a reversible process…

\[
\begin{align*}
T_h - dT & \quad -dQ \\
T_c + dT & \quad +dQ
\end{align*}
\]

And, the total entropy change for this $dT$ change is positive!

\[
dS_{tot} = dS_{hot} + dS_{cold} \quad \text{eng conservation}
\]

\[
dS_{tot} = \frac{-m_i c_i dT}{T_h} + \frac{+m_w c_w dT}{T_c} = \frac{-dQ}{T_h} + \frac{+dQ}{T_c} = dQ \left( -\frac{1}{T_h} + \frac{1}{T_c} \right) > 0 \quad (\text{since } T_h > T_c)
\]

Note: Individually, $S$ can be calculated by independent surrogate quasi-static processes raising and decreasing $T$ slowly.
Example of an Irreversible Mixing Process

To be more concrete,

From 1\textsuperscript{st} Law, we can solve for $T_{\text{final}}$ from below:

$$m_{\text{iron}} c_{\text{iron}} \left( T_{\text{final}} - T_h \right) + m_{\text{water}} c_{\text{water}} \left( T_{\text{final}} - T_c \right) = 0$$

And, $\Delta S_{\text{tot}} = \Delta S_h + \Delta S_c$

$$= m_{\text{iron}} c_{\text{iron}} \ln \left( \frac{T_{\text{final}}}{T_h} \right) + m_{\text{water}} c_{\text{water}} \ln \left( \frac{T_{\text{final}}}{T_c} \right)$$

$$= -m_{\text{iron}} c_{\text{iron}} \ln \left( \frac{T_h}{T_{\text{final}}} \right) + m_{\text{water}} c_{\text{water}} \ln \left( \frac{T_{\text{final}}}{T_c} \right)$$

$$> 0$$

Although it is not obvious from this expression that $\Delta S_{\text{tot}} > 0$, we know that it will be so from our argument on the previous page!

Let calculate …
Example 20.10

1.00kg of water at 100°C is placed in thermal contact with 1.00kg of water at 0°C.

First, we can solve for $T_f$:

$$mc_w(T_{final} - T_h) + mc_w(T_{final} - T_c) = 0 \rightarrow T_{final} = \frac{T_h + T_c}{2} = 50^\circ C$$

Now, $\Delta S_{tot} = \Delta S_h + \Delta S_c$

$$= mc_w \ln\left(\frac{T_{final}}{T_h}\right) + mc_w \ln\left(\frac{T_{final}}{T_c}\right)$$

$$= 1.00kg \left(\frac{4190 \text{ J}}{\text{kg} \cdot \text{K}}\right) \left(\ln\left(\frac{50 + 273}{100 + 273}\right) + \ln\left(\frac{50 + 273}{273}\right)\right)$$

$$= 4190 \text{ J/} K \left(-0.1439 + 0.1682\right) = +102 \text{ J/} K > 0$$
**Microscopic Interpretation of Entropy**

**Microstate vs. Macrostate:**

<table>
<thead>
<tr>
<th>Macroscopic state</th>
<th>Corresponding microscopic states</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two heads, two tails</td>
<td><img src="image1" alt="Microscopic states" /></td>
</tr>
<tr>
<td>Four heads</td>
<td><img src="image2" alt="Microscopic states" /></td>
</tr>
<tr>
<td>Three heads, one tails</td>
<td><img src="image3" alt="Microscopic states" /></td>
</tr>
<tr>
<td>One head, three tails</td>
<td><img src="image4" alt="Microscopic states" /></td>
</tr>
<tr>
<td>Four tails</td>
<td><img src="image5" alt="Microscopic states" /></td>
</tr>
</tbody>
</table>

Recall:

**Macrostate:** a bulk description of a system in terms of its macroscopic variables.
Microscopic Interpretation of Entropy

Observations:

1. For a given macrostate, typically there are many possible microstates!
   
   (If the # of coins (or molecules) is large (~ $N_A$), the # of microstates corresponding to a particular macrostate can be astronomically large.)

2. All individual microstates are equally likely.

   (Each coin has exactly 50% being head or tail and each toss is independent.)
Microscopic Interpretation of Entropy

Observations:

3. However, for a given macrostate, the # of possible microstates are different!
   (Since all microstates are equally likely, the probability for different macrostates is different.)

4. Some macrostate are much more probable than others.
   (When $N \sim N_A$, this disparity is much much larger!)
Microscopic Interpretation of Entropy

Observations:

5. The *less probable* macrostates (all heads or all tails) correspond to *more ordered* microstates!

6. The *more probable* macrostates (50/50 heads and tails) correspond to the more *disordered* microstates.
Microscopic Interpretation of Entropy

These observations motivate the following microscopic definition of entropy:

\[ S = k \ln W \]

Boltzmann’s Equation

where \( W \) is the \# of possible microstates for a given macrostate and \( k \) is the Boltzmann constant.

Example (4 coins):

- macrostate (all heads)
  - \# of microstates = 1
  - \( S = k \ln 1 = 0 \)
  - All matched coins (ordered)

- macrostate (3 H & 1 T)
  - \# of microstates = 4
  - \( S = k \ln 4 \)
  - unmatched coins (less order)