Chapter 20: Entropy and the Second Law of Thermodynamics

The Conservation of Energy law allows energy to flow bi-directionally between its various forms. For example in a pendulum, energy continually goes to/from kinetic energy and potential energy.

Consider putting some ice into a glass of water.

Conservation of energy would allow:
• ice getting colder and water getting hotter.
• ice getting warmer and water getting cooler.
• both ice and water staying at their initial temperatures.

Only one of these scenarios happens, so something must be controlling the direction of energy flow.

That direction is set by a quantity called entropy.
Entropy

Entropy has its roots in Quantum Mechanics. It is a measure of the available quantum states to a system. -- Or in other words, a measure of the order (or disorder) of a system. Mathematically related to probability.

Consider a deck of (shuffled) playing cards. Five cards are selected at random. Each 5-card combination is called a microstate and has an equal probability of occurring.

Prob any five card combination = \((52)*(51)*(50)*(49)*(48) = 311,875,200\)

Prob Royal diamond flush = \(1/(52)*(51)*(49)*(48) = 3.206\times10^{-9}\)

Prob ace of clubs = \(9.615\times10^{-2}\)
**Entropy**

Let’s bring the numbers down to illustrate the relationship between entropy and probability.

Consider an insulated box containing six molecules (N=6). The box is divided into the left half and the right half. Let $n_1$ be the number of molecules in the left half and $n_2$ be the number of molecules in the right half.

Note: $N = n_1 + n_2$

We now selectively pick molecules to be placed in the left half.  

1\textsuperscript{st} molecule we can pick any of the six available molecules. 
2\textsuperscript{nd} molecule we can pick any of the five remaining molecules. 

etc.......

Total number of ways we can select the six molecules = $6! = 720$

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**Entropy**

Molecules do not come with name tags (i.e., they are **indistinguishable**), so the order doesn’t matter.

In Figure a, there are $4! (=24)$ different ways we could have selected the four molecules for the left side and $2! (=2)$ different ways we could have left the other two molecules in the right half.

Multiplicity $W$ is the resulting number of microstates.

$$W = \frac{N!}{n_1! n_2!} \quad W_{\text{III}} = \frac{6!}{4! 2!} = \frac{720}{24 \cdot 2} = 15$$

Note: $0! = 1$ and $6! = 6 \cdot 5 \cdot 4 \cdot 3 \cdot 2 \cdot 1 = 720$
Entropy

Continuing with all possible combinations of the six molecules in the two halves:

<table>
<thead>
<tr>
<th>Label</th>
<th>$n_1$</th>
<th>$n_2$</th>
<th>Multiplicity $W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>6</td>
<td>0</td>
<td>$6!/(6!0!) = 1$</td>
</tr>
<tr>
<td>II</td>
<td>5</td>
<td>1</td>
<td>$6!/(5!1!) = 6$</td>
</tr>
<tr>
<td>III</td>
<td>4</td>
<td>2</td>
<td>$6!/(4!2!) = 15$</td>
</tr>
<tr>
<td>IV</td>
<td>3</td>
<td>3</td>
<td>$6!/(3!3!) = 20$</td>
</tr>
<tr>
<td>V</td>
<td>2</td>
<td>4</td>
<td>$6!/(2!4!) = 15$</td>
</tr>
<tr>
<td>VI</td>
<td>1</td>
<td>5</td>
<td>$6!/(1!5!) = 6$</td>
</tr>
<tr>
<td>VII</td>
<td>0</td>
<td>6</td>
<td>$6!/(0!6!) = 1$</td>
</tr>
</tbody>
</table>

The most likely state (highest probability) is the state with the greatest multiplicity, $W_{IV}$ with three molecules in each half (most disordered).

Entropy

So, ... How does this play out in Thermodynamics?

Entropy is the Boltzmann constant ($k = 1.38 \times 10^{-23}$ J/K) times the natural log of $W$.

$$S = k \ln W$$

Temperature can now be defined in terms of energy $E$ and entropy $S$!!

$$T \equiv \left( \frac{\partial E}{\partial S} \right)_N$$

We’ll save that for a later course, though........
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But what about the ice?
The ice is a very ordered state with all of the molecules in specific locations in the crystal. *(W small)*

Liquid water has many states for the water molecules. *(W large)*

Nature will maximize number of energetically-allowed microstates.
Thus, heat (energy) always flows from the water to the ice.

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**Relationship between entropy and heat**

*Entropy is a state property* (like internal energy and temperature). It does not depend on the process, only depends on the initial and final states.

**Define the change in entropy to be:**

\[ \Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} \]

Q: energy transferred as heat
T: temperature in Kelvin

sign of $\Delta S$ and $Q$, SI unit of $S$: J/K
Reversible and Irreversible Processes

An irreversible process is one that cannot be reversed by means of small changes in the environment. Entropy increases. $\Delta S > 0$

e.g. A broken egg cannot go back to being a whole egg. Heat does not transfer from the ice to the water though it would not violate the law of energy conservation.

Note: ALL real processes are irreversible!

If an irreversible process occurs in a closed system, the entropy $S$ of the system always increases, it never decreases. (entropy postulate)

*Everything* you do will increase the entropy of the universe! $\Delta S \geq 0$

Second Law of Thermodynamics

$\Delta S = 0$ reversible process; $\Delta S > 0$ irreversible process
Example with the ice and water

Suppose 0.1 kg ice at 0°C (273K) is in 0.5 kg water at 20°C (293K).

Calculate Heat transfers:

\[
Q_{\text{melt}} = m_{\text{ice}}L_f = (0.1\text{kg})(3.33\times10^5\text{J/kg}) = 3.33\times10^4\text{J}
\]

\[
Q_{\text{water}} = m_{\text{water}}c_w\Delta T \\
\Delta T = Q_{\text{water}}/m_{\text{water}}c_w = -15.9\text{K}
\]

\[
Q_{\text{water}} = m_{\text{water}}c_w(277.1 - T_f) = m_{\text{ice}}c_w(T_f - 273)
\]

\[
T_f = (277.1m_{\text{water}} + 273m_{\text{ice}})/(m_{\text{ice}} + m_{\text{water}}) = 276.4\text{K}
\]

What is the change in entropy of the ice as it melts at 0°C?

Convert all temperatures into Kelvin!!

\[
\Delta S_{\text{melt}} = S_f - S_i = \int_{T_i}^{T_f} \frac{dQ}{T} = \frac{m_{\text{ice}}L_f}{T}
\]

\[
= \frac{(0.1\text{kg})(3.33\times10^5\text{J/kg})}{273\text{K}} = +122.0\text{J/K}
\]
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Example with the ice and water

Suppose 0.1 kg ice at 0°C (273K) is in 0.5 kg water at 20°C (293K).

What is the change in entropy of the ice water as it warms up to the final temperature?

\[ \Delta S_{\text{ice-water}} = S_f - S_i = \int_{i}^{f} \frac{dQ}{T} = \int_{i}^{f} \frac{m_{\text{ice-water}} c_{w} dT}{T} = m_{\text{ice-water}} c_{w} \int_{i}^{f} \frac{dT}{T} \]

\[ = m_{\text{ice-water}} c_{w} \ln \left( \frac{T_f}{T_i} \right) = (0.1 \text{ kg})(4186 \text{ J/kg-K}) \ln \left( \frac{273.4 \text{ K}}{273 \text{ K}} \right) = +5.2 \text{ J/K} \]

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Example with the ice and water

Suppose 0.1 kg ice at 0°C (273K) is in 0.5 kg water at 20°C (293K).

What is the change in entropy of the water as it melted the ice?

\[ \Delta S_{\text{water-melt}} = S_f - S_i = \int_{i}^{f} \frac{dQ}{T} = \int_{i}^{f} \frac{m_{\text{water}} c_{w} dT}{T} = m_{\text{water}} c_{w} \int_{i}^{f} \frac{dT}{T} \]

\[ = m_{\text{water}} c_{w} \ln \left( \frac{T_f}{T_i} \right) = (0.5 \text{ kg})(4186 \text{ J/kg-K}) \ln \left( \frac{277.1 \text{ K}}{293 \text{ K}} \right) = -116.8 \text{ J/K} \]
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Example with the ice and water

Suppose 0.1 kg ice at 0°C (273K) is in 0.5 kg water at 20°C (293K).

What is the change in entropy of the water as it cooled down to the final temperature?

\[
\Delta S_{\text{water cooled}} = S_f - S_i = \int_i^f \frac{dQ}{T} = \int_i^f \frac{m_{\text{water}} c_w}{T} \, dT = m_{\text{water}} c_w \ln \left( \frac{T_f}{T_i} \right)
\]

\[
= m_{\text{water}} c_w \ln \left( \frac{T_f}{T_i} \right) = (0.5 \text{kg})(4186 \text{ J/kg·K}) \ln \left( \frac{276.4 \text{ K}}{277.1 \text{ K}} \right) = -5.3 \text{ J/K}
\]

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Example with the ice and water

Suppose 0.1 kg ice at 0°C (273K) is in 0.5 kg water at 20°C (293K).

Total change in entropy of the ice / water system as it came to thermal equilibrium

\[
\Delta S_{\text{total}} = \Delta S_{\text{melt}} + \Delta S_{\text{ice water}} + \Delta S_{\text{water melt}} + \Delta S_{\text{water cooled}}
\]

\[
= (+122.0) + 5.2 + (-116.8) + (-5.3) \text{ J/K}
\]

\[
= +5.1 \text{ J/K}
\]
**ΔS for free expansion**

**Free expansion is an irreversible process.** Problem: no clear relation between \( Q \) and \( T \) that allows us to calculate \( \Delta S = \int_{i}^{f} \frac{dQ}{T} \).

Since entropy is a state function, we can calculate \( \Delta S \) from a **reversible process which has the same initial and final state**.

For free expansion, \( T_i = T_f \). So we can use a reversible isothermal process (\( T = \text{constant} \)) with the same initial and final state to calculate \( \Delta S \).

\[
\Delta S = S_f - S_i = \frac{1}{T} \int_{i}^{f} dQ = \frac{Q}{T}
\]

In isothermal expansion, \( Q > 0 \), therefore \( \Delta S > 0 \) that means \( \Delta S > 0 \) for free expansion.

For a process that \( \Delta T \) is small compared to \( T \):

\[
\Delta S = S_f - S_i \approx \frac{Q}{T_{\text{avg}}}
\]
my goodness........ It’s December already!!

Water is heated on a stove. Which of the following temperature changes results in the greatest change in entropy?

(1) from 10°C to 20°C
(2) from 45°C to 55°C
(3) from 80°C to 90°C
(4) all have the same entropy change.

\[
\Delta S_{\text{water}} = \int \frac{dQ}{T} = \int \frac{m_{\text{water}} c_w dT}{T} = m_{\text{water}} c_w \int \frac{dT}{T} = m_{\text{water}} c_w \ln \left( \frac{T_f}{T_i} \right)
\]

Water is heated on a stove. Which of the following temperature changes results in the greatest change in entropy?

(1) from 10°C to 20°C  =>  283K to 293K  =>  ln(293/283) = 0.035
(2) from 45°C to 55°C  =>  318K to 328K  =>  ln(328/318) = 0.031
(3) from 80°C to 90°C  =>  353K to 363K  =>  ln(363/353) = 0.028
(4) all have the same entropy change.
**The Second Law of Thermodynamics**

For the free expansion, we have $\Delta S > 0$. It is an irreversible process in a closed system.

For the reversible isothermal process, for the gas $\Delta S > 0$ for expansion and $\Delta S < 0$ for compression. However, the gas itself is not a closed system. It is only a closed system if we include both the gas and the reservoir.

During expansion:

$$\Delta S_{\text{gas}} = \frac{|Q|}{T} \quad \Delta S_{\text{res}} = -\frac{|Q|}{T}$$

So: $\Delta S_{\text{total}} = 0$

$$\Delta S \geq 0 \quad (\text{Second Law of Thermodynamics})$$

If a process occurs in a closed system, the entropy of the system increases for irreversible processes and remains constant for reversible processes. It never decreases.

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**Friday: Entropy in real world -- Engines**

![Diagram of an engine](image)