Second Law of Thermodynamics:

$$\Delta S_{\text{UNIV}} = \Delta S_{\text{SYS}} + \Delta S_{\text{SURR}} \geq 0$$

The net entropy will increase or stay the same. It will never decrease.

$$\Delta S_{\text{SURR}} > 0 \quad \Delta S_{\text{SURR}} \geq \frac{q}{T}$$

$$\Delta S_{\text{UNIV}} = 0 \quad \text{only for a reversible process}$$

$$\Delta S_{\text{UNIV}} > 0 \quad \text{for all other processes}$$

Atkins: The entropy of the universe tends to increase.
\( \Delta S_{\text{univ}} \) is pathway dependent:

**Irreversible expansion**

\[
w = -P_2 \Delta V = -1.42 \text{ kJ}
\]

\[
q = -w = 1.42 \text{ kJ}
\]

\( P_1 = 15 \text{ atm} \)

\( V_1 = 1 \text{ L} \)

\( T = 298 \text{ K} \)

\( P_2 = 1 \text{ atm} \)

\( V_2 = 15 \text{ L} \)

\( T = 298 \text{ K} \)

\[
\Delta S_{\text{sys}} = 13.8 \text{ J K}^{-1}
\]

\[
\Delta S_{\text{surr}} = -4.8 \text{ J K}^{-1}
\]

\[
\Delta S_{\text{univ}} = 9 \text{ J K}^{-1}
\]

**Reversible expansion**

\[
w = -nRT \ln \left( \frac{V_2}{V_1} \right) = -4.12 \text{ kJ}
\]

\[
q_{\text{rev}} = -w_{\text{rev}} = 4.12 \text{ kJ}
\]

\( P_1 = 15 \text{ atm}, V_1 = 1 \text{ L} \)

\( P_2 = 1 \text{ atm}, V_2 = 15 \text{ L} \)

\[
\Delta S_{\text{sys}} = 13.8 \text{ J K}^{-1}
\]

\[
\Delta S_{\text{surr}} = -4.8 \text{ J K}^{-1}
\]

\[
\Delta S_{\text{univ}} = 0 \text{ J K}^{-1}
\]
Isothermal compression is pathway dependent:

Reversible compression

\[ w = -P_1 \Delta V = 21.3 \text{ kJ} \]
\[ q = -w = -21.3 \text{ kJ} \]

Irreversible compression

\[ w = -nRT \ln \left( \frac{V_1}{V_2} \right) = 4.12 \text{ kJ} \]
\[ q_{\text{rev}} = -w_{\text{rev}} = -4.12 \text{ kJ} \]

\[ \Delta S_{\text{sys}} = -13.8 \text{ J K}^{-1} \]
\[ \Delta S_{\text{surr}} = 71.4 \text{ J K}^{-1} \]
\[ \Delta S_{\text{univ}} = 57.6 \text{ J K}^{-1} \]
Corollary: For an isolated system $\Delta S_{\text{SYS}} \geq 0$

A gas will not spontaneously compress.

Spontaneous $\Delta S = 27.7 \text{ k}$

Will not happen $\Delta S = -27.7 \text{ k}$

Heat will not flow spontaneously from a cooler to a warmer object.

$\Delta S_1 = \frac{q}{T_1}$  $\Delta S_2 = \frac{-q}{T_2}$

$\Delta S_{\text{SYS}} = \Delta S_1 + \Delta S_2 = \frac{q}{T_1} + \frac{-q}{T_2} = q \left( \frac{T_2 - T_1}{T_1 T_2} \right) < 0$

$T_1 > T_2$

$q$ small $\Rightarrow T_1, T_2 \approx \text{constant}$

$\Delta S_{\text{SYS}} < 0$ violating the second law

$\therefore \text{it will not happen}$

Number of molecules

$W_{\text{Left}} = (0.25)^{20} = 9.09 \times 10^{-13}$

$W_{\text{Right}} = (1)^{20} = 1$

in a truly macroscopic system $N \approx 10^{23}$
Second Law of Thermodynamics:

“The second law of thermodynamics has as much truth as saying that, if you poured a glass of water into the ocean, it would not be possible to get the same glass of water back again”

James Clerk Maxwell (1831-1879)
In a constant pressure process (most of real life):

\[ \Delta H = q_p \quad \therefore \Delta S = \frac{\Delta H}{T} \]

Consider the entropy change associated with the melting of an ice cube at \( T = 273.15 \).  

\[ \Delta S = \frac{n \Delta_{\text{fus}} H^\ominus}{T} \]

\[ \frac{\Delta S}{n} = \frac{\Delta_{\text{fus}} H^\ominus}{T} = \frac{6.01 \, \text{kJ mol}^{-1}}{273.15 \, \text{K}} \quad \Delta S = 22.0 \, \text{J K}^{-1} \, \text{mol}^{-1} \]

What if the temperature changes during an expansion, reaction or phase transition?

\[ dS = \frac{dH}{T} \quad dH = dq_p = C_p \, dT \quad \therefore \Delta S = \int_{T_1}^{T_2} \frac{C_p \, dT}{T} \]
1. Calculate the final temperature assuming adiabatic mixing (i.e. no heat transfer to or from surroundings).

2. Calculate the entropy change for A, B and the whole system.

The heat capacity of chlorine gas is given by:

\[ C_p = (31.0 + 0.008 T) \text{ J K}^{-1} \text{ mol}^{-1} \]

Calculate ΔS when 2.00 moles of Cl₂ (g) are heated from 300K to 400K at constant pressure.
Spontaneity:

When will a chemical reaction occur spontaneously?

Endothermic, exothermic and energy neutral processes all may occur spontaneously. \( \Delta H_{\text{sys}} \) and \( \Delta U_{\text{sys}} \) do not control spontaneity.

\[ \Delta S_{\text{UNIV}} = \Delta S_{\text{SYS}} + \Delta S_{\text{SURR}} \geq 0 \]

Second Law

\[ \Delta S_{\text{SYS}} = \Delta_r S \]

\[ \Delta S_{\text{SURR}} = \frac{q_p}{T} = -\frac{\Delta_r H}{T} \]

\[ \Delta S_{\text{UNIV}} = \Delta_r S - \frac{\Delta_r H}{T} \geq 0 \]

A reaction is spontaneous if and only if:

\[ \Delta_r S > \frac{\Delta_r H}{T} \]
<table>
<thead>
<tr>
<th>Enthalpy</th>
<th>Entropy</th>
<th>Exothermic?</th>
<th>Spontaneous?</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta_r H &gt; 0$</td>
<td>$\Delta r S &lt; 0$</td>
<td>Endothermic “heat required”</td>
<td>NO $\Delta S_{UNIV} &lt; 0$</td>
</tr>
<tr>
<td>$\Delta r H &lt; 0$</td>
<td>$\Delta r S &gt; 0$</td>
<td>Exothermic “heat released”</td>
<td>YES $\Delta S_{UNIV} &gt; 0$</td>
</tr>
<tr>
<td>$\Delta r H &gt; 0$</td>
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</tr>
<tr>
<td>$\Delta r H &lt; 0$</td>
<td>$\Delta r S &lt; 0$</td>
<td>Exothermic “heat released”</td>
<td>IF $-\Delta r H &gt; -\Delta r S / T$ Enthalpy Driven</td>
</tr>
</tbody>
</table>

**Energy must be conserved**

First Law

**But ...**

**Entropy Rules!**

Second Law
Standard Entropy of Reaction:

\[ \Delta_R S^\Theta = \sum S^\Theta_{\text{(Prod.)}} - \sum S^\Theta_{\text{(React.)}} \]

Sample Problem:

Calculate the change in entropy and change in enthalpy for the combustion of ten grams of table sugar (sucrose) at 298 K. How does this compare with the information on the label?

Sample Problem:

Consider the following reaction: \( \frac{3}{2} \text{O}_2(\text{g}) + 2 \text{Fe} (\text{s}) \rightarrow \text{Fe}_2\text{O}_3 (\text{s}) \)

Calculate \( \Delta S_{\text{SYS}} \), \( \Delta S_{\text{SURR}} \), and \( \Delta S_{\text{UNIV}} \).