For steam → water

\[ \Delta S_{\text{tot}} = + \frac{(40.65 \times 10^3 \text{ J/mol})}{T} - 108.9 \text{ J/(mol K)} \]

At \( T = 100 ^\circ C \), \( \Delta S_{\text{tot}} \) evaluates to...

<table>
<thead>
<tr>
<th>Option</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>&lt; 0</td>
</tr>
<tr>
<td>2.</td>
<td>= 0</td>
</tr>
<tr>
<td>3.</td>
<td>&gt; 0</td>
</tr>
</tbody>
</table>

A non-chemistry question

With apologies for a question not related to our course, ...

if you are taking a course in linear algebra, or plan on doing so soon, ...

please email Dan Dill, dan@bu.edu, with subject line “linear algebra”.

Thank you.
Taking stock

Spontaneity means that ...
\[ \Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \]

Spontaneity does not require that ...
\[ \Delta S_{\text{sys}} > 0 \text{ or } \Delta S_{\text{surr}} > 0 \]

A neat illustration of the separate roles of \( \Delta S_{\text{sys}} \) and \( \Delta S_{\text{surr}} \) is understanding why steam condenses and water boils.

[Quiz] For steam \( \rightarrow \) water, which of the following must be true?

- 17% 1. \( \Delta S_{\text{tot}} < 0 \)
- 17% 2. \( \Delta S_{\text{tot}} = 0 \)
- 17% 3. \( \Delta S_{\text{sys}} > 0 \)
- 17% 4. \( \Delta S_{\text{sys}} < 0 \) and \( \Delta S_{\text{surr}} < 0 \)
- 17% 5. \( \Delta S_{\text{sys}} < 0 \) and \( \Delta S_{\text{surr}} = 0 \)
- 17% 6. \( \Delta S_{\text{sys}} < 0 \) and \( \Delta S_{\text{surr}} > 0 \)

For steam \( \rightarrow \) water at 94 °C

Super cooled steam at 94 °C condenses spontaneously to water.
Spontaneity means \( \Delta S_{\text{tot}} > 0 \)
But "gas \( \rightarrow \) liquid" means \( \Delta S_{\text{sys}} < 0 \)
This means it must be \( \Delta S_{\text{surr}} \) that makes \( \Delta S_{\text{tot}} > 0 \)
How to get \( \Delta S_{\text{surr}} \)?
The trick: \( \Delta S_{\text{surr}} = \Delta H_{\text{surr}} / T = -\Delta H_{\text{sys}} / T \)
Hence we can always write \( \Delta S_{\text{tot}} = \Delta S_{\text{surr}} + \Delta S_{\text{sys}} \) as
\[ \Delta S_{\text{tot}} = -\left( \Delta H_{\text{sys}} / T \right) + \Delta S_{\text{sys}} \]
[TP] For steam $\rightarrow$ water

$$\Delta S_{\text{net}} = + \frac{(40.65 \times 10^3 \text{ J/mol})}{T} - 108.9 \text{ J/(mol K)}$$

At $T = 100 \degree C$, $\Delta S_{\text{net}}$ evaluates to ...

0% 1. < 0
0% 2. = 0
0% 3. > 0

[TP] For steam $\rightarrow$ water

$$\Delta S_{\text{net}} = + \frac{(40.65 \times 10^3 \text{ J/mol})}{T} - 108.9 \text{ J/(mol K)}$$

At $T = 94 \degree C$, $\Delta S_{\text{net}}$ evaluates to ...

33% 1. < 0
33% 2. = 0
33% 3. > 0

[Quiz] For steam $\rightarrow$ water, which of the following must be true?

17% 1. $\Delta S_{\text{sys}} < 0$
17% 2. $\Delta S_{\text{sys}} = 0$
17% 3. $\Delta S_{\text{sys}} > 0$
17% 4. $\Delta S_{\text{sys}} < 0$ and $\Delta S_{\text{sur}} < 0$
17% 5. $\Delta S_{\text{sys}} < 0$ and $\Delta S_{\text{sur}} = 0$
17% 6. $\Delta S_{\text{sys}} < 0$ and $\Delta S_{\text{sur}} > 0$
Taking stock

Spontaneity means that...

\[ \Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} > 0 \]

Spontaneity does not require that...

\[ \Delta S_{\text{sys}} > 0 \text{ or } \Delta S_{\text{sur}} > 0 \]

A neat illustration of the separate roles of \( \Delta S_{\text{sys}} \) and \( \Delta S_{\text{sur}} \) is understanding why steam condenses and water boils.

The same approach works for melting and for sublimation.

\[ \Delta S \] and freezing point depression

Make a diagram of \( S \) (vertical axis) for liquid and solid water (ice).

Connect the two entropies with an arrow corresponding to liquid \( \rightarrow \) solid.

What is the length of the arrow?

\[ \Delta S \] and freezing point depression

How is \( S \) (liquid) changed by adding a small amount of solute?

What must happen to the length of the arrow connecting the water solution to pure ice?

How can this change come about?
How to determine $\Delta S_{\text{sys}}$ for a chemical reaction?

We have seen that we can get $\Delta S_{\text{sys}}$ for a phase transition using $\Delta S_{\text{tot}} = 0$ at the transition temperature.

Getting $\Delta S_{\text{sys}}$ for a chemical reaction requires a different approach.

In principle we could get $\Delta S_{\text{sys}}$ by analyzing changes in particle and energy dispersal in the reaction.

But, in practice, it is easier to get $\Delta S_{\text{sys}}$ by measuring heat flow between system and surroundings when they are in equilibrium.

At equilibrium, $\Delta S_{\text{tot}} = 0$, and so ...

$$\Delta S_{\text{sys}} = -\Delta S_{\text{tot}} = -\Delta H_{\text{sys}} / T = +\Delta H_{\text{sys}} / T$$