

Slides on Spontaneity of phase transitions: water \rightleftharpoons steam, CH102 Spring 2016, A1 and A2 lecture 29 Copyright © 2016 Dan Dill dan@bu.edu

Spontaneity of phase transitions: water \rightleftharpoons steam
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Taking stock

Spontaneity **means** that ...
 $\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} > 0$

Spontaneity **does not** require that ...
 $\Delta S_{\text{sys}} > 0$ or $\Delta S_{\text{sur}} > 0$

A neat illustration of the **separate roles** of ΔS_{sys} and ΔS_{sur} is understanding why **steam condenses** and **water boils**

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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 ΔS_{sur} that makes $\Delta S_{\text{tot}} > 0$

How to get ΔS_{sur} ?

The trick: $\Delta S_{\text{sur}} = \Delta H_{\text{sur}} / T = -\Delta H_{\text{sys}} / T$

Hence we can always write $\Delta S_{\text{tot}} = \Delta S_{\text{sur}} + \Delta S_{\text{sys}}$ as

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

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steam \rightarrow water at 94 °C

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

At 100 °C, steam and water are **in equilibrium**, so ...

$$\Delta S_{\text{tot}} = 0 = +\Delta H_{\text{vap}} / (373 \text{ K}) + \Delta S_{\text{sys}}$$

From this we know that ΔS_{sys} ...

$$= -\Delta H_{\text{vap}} / (373 \text{ K})$$
$$= -(40.65 \times 10^3 \text{ J/mol}) / (373 \text{ K}) = -108.9 \text{ J/(mol K)}$$

For **other temperatures** ΔS_{tot} ...

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

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[TP] For steam \rightarrow water
 $\Delta S_{\text{tot}} = + (40.65 \times 10^3 \text{ J/mol})/T - 108.9 \text{ J/(mol K)}$
 At $T = 94^\circ\text{C}$, ΔS_{tot} evaluates to ...

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

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[TP] For steam \rightarrow water
 $\Delta S_{\text{tot}} = + (40.65 \times 10^3 \text{ J/mol})/T - 108.9 \text{ J/(mol K)}$
 At $T = 100^\circ\text{C}$, ΔS_{tot} evaluates to ...

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

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[TP] For steam \rightarrow water
 $\Delta S_{\text{tot}} = + (40.65 \times 10^3 \text{ J/mol})/T - 108.9 \text{ J/(mol K)}$
 At $T = 106^\circ\text{C}$, ΔS_{tot} evaluates to ...

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

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steam \rightarrow water at 94°C

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

The graph shows ΔS_{tot} (J/(mol K)) on the y-axis and T ($^\circ\text{C}$) on the x-axis. The y-axis ranges from -1 to 2, and the x-axis ranges from 92 to 104. A blue line with a negative slope represents the equation $\Delta S_{\text{tot}} = + 40.65 \times 10^3 / T - 108.9$. A red dot is plotted at $T = 94^\circ\text{C}$ and $\Delta S_{\text{tot}} \approx 1.8$. A green dot is plotted at $T = 100^\circ\text{C}$ and $\Delta S_{\text{tot}} = 0$. A vertical red line connects the red dot to the x-axis at 94.

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