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Spontaneity of phase transitions: water ⇌ steam

CH102 Spring 2016, A1 and A2 lecture 29

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Taking stock

Spontaneity means that …

$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{sur} > 0$

Spontaneity does not require that …

$\Delta S_{sys} > 0$ or $\Delta S_{surr} > 0$

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

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steam → water at 94 °C

Super cooled steam at 94 °C condenses spontaneously to water.

Spontaneity means $\Delta S_{tot} > 0$

But "gas → liquid" means $\Delta S_{sys} < 0$

This means it must be ΔS_{sur} that makes $\Delta S_{tot} > 0$

How to get ΔS_{sur}?

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

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

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

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steam → water at 94 °C

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

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

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

From this we know that ΔS_{sys} …

$= -\Delta H_{vap} / (373\ \text{K})$

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

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 → water

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

At $T = 94\ ^{o}\text{C}$, ΔS_{tot} evaluates to ...

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

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[TP] For steam → water

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

At $T = 100\ ^{o}\text{C}$, ΔS_{tot} evaluates to ...

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

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[TP] For steam → water

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

At $T = 106\ ^{o}\text{C}$, ΔS_{tot} evaluates to ...

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

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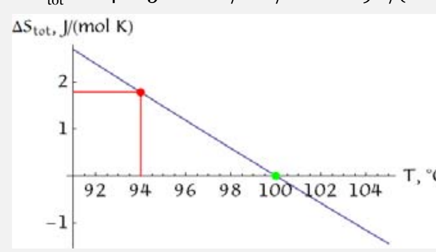
steam → water at 94 ºC

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

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



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