[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 ...

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

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Response Counter

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Lecture 33 CH102 A1 (MWF 9:05 am)

Wednesday, April 19, 2017

- Spontaneity of phase transitions: water ⇌ steam
- ΔS picture colligative properties: Freezing point depression

Next lecture: Absolute entropy. Entropy change of reaction. System-only measure of total entropy change: ΔG. Using temperature to change spontaneity: ΔG versus T. The three faces of ΔG. Using temperature to change equilibrium: K versus T.

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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.

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Spontaneity of phase transitions

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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

[Quiz] For steam → water, which of the following must be true?

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

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

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

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 ...

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

From this we know that ΔS_{sys} ...

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

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

For other temperatures ΔS_{tot} ...

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

[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 $T = 94\ ^{o}\text{C}$, 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 $T = 106\ ^{o}\text{C}$, ΔS_{tot} evaluates to ...

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

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[Quiz] For steam → water, which of the following must be true?

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

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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

The same approach works for melting and for sublimation

The role of ΔS in colligative properties

ΔS 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 → solid.

What is the length of the arrow?

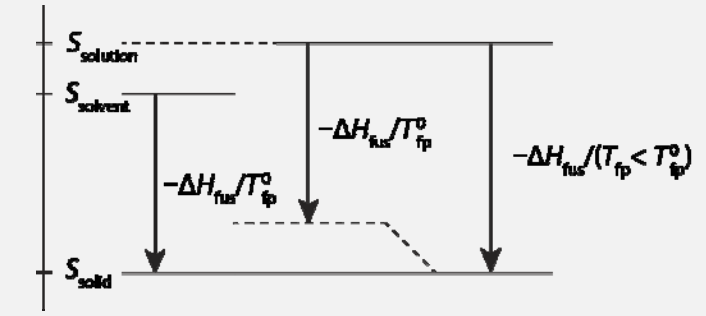
ΔS and freezing point depression

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?

ΔS and freezing point depression



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ΔS and colligative properties

Each of the four colligative properties can be understood in terms of entropy changes.

See the notes on colligative properties at ...

http://quantum.bu.edu/courses/ch102-spring-2017/handouts.html

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How to determine ΔS_{sys} for a chemical reaction?

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

Getting ΔS_{sys} for a chemical reaction requires a different approach.

In principle we could get ΔS_{sys} by analyzing changes in particle and energy dispersal in the reaction.

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

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

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

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