

Lecture 33 CH102 A1 (MWF 9 am) Spring 2017 Copyright © 2017 Dan Dill dan@bu.edu

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

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

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Lecture 33 CH102 A1 (MWF 9:05 am)

Wednesday, April 19, 2017

- Spontaneity of phase transitions: water \rightleftharpoons 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 ...

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

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 ΔS_{sys} and ΔS_{surr} is understanding why **steam condenses** and **water boils**

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[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. $\Delta S_{\text{tot}} > 0$
 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 $\Delta S_{\text{surr}} > 0$

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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_{surr} that makes $\Delta S_{\text{tot}} > 0$

How to get ΔS_{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

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

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

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

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

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[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. $\Delta S_{\text{tot}} > 0$
 17% 4. $\Delta S_{\text{sys}} < 0$ and $\Delta S_{\text{sur}} < 0$
 17% 5. $\Delta S_{\text{sys}} < 0$ and $\Delta S_{\text{sur}} = 0$
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Taking stock

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

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**

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$$\Delta S = \Delta H / T = -\Delta H / T$$

The role of ΔS in colligative properties

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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 \rightarrow solid.

What is the length of the arrow?

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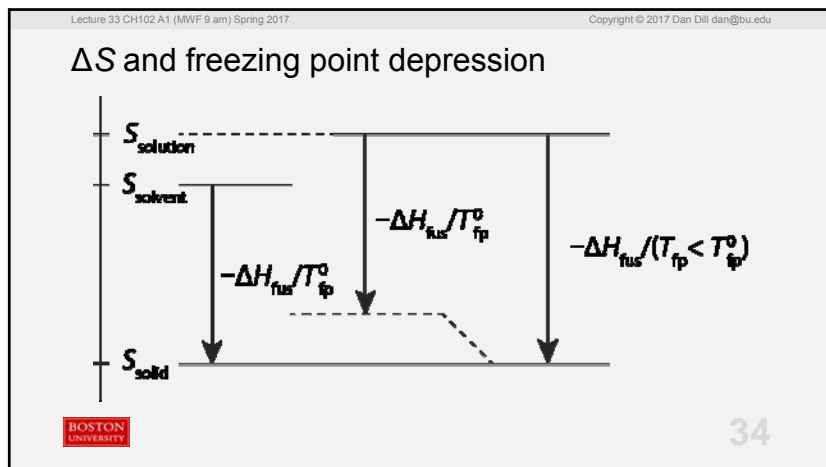
ΔS and freezing point depression

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?

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

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

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