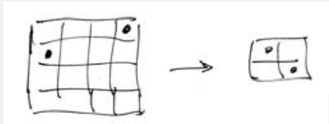
[TP] The sketch illustrates gas → liquid. $\Delta S_{\mathrm{sys}}/k_{\mathrm{B}}$ for this process is …

20% 1. ln(5)
20% 2. ln(11)
20% 3. ln(1/9)
20% 4. Something else.
20% 5. Further information needed.



BOSTON UNIVERSITY 1

Lecture 30 CH102 A2 (MWF 11:15 am)

Monday, April 9, 2018

- Complete: Spontaneity of phase transitions: water ⇌ steam
- ΔS in colligative properties: Freezing point depression
- Absolute entropy

Next lecture: Entropy change of reaction. Free energy change, ΔG. $\Delta G, E, \Delta H, \Delta S, Q, K$, and T: Connection between T and K.

Colligative properties in terms of entropy change
http://quantum.bu.edu/courses/ch102-spring-2018/handouts.html

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[TP] The sketch illustrates gas → liquid. $\Delta S_{\mathrm{sys}}/k_{\mathrm{B}}$ for this process is …

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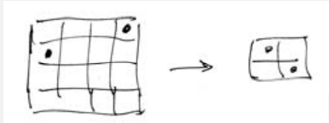

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steam → water at 94 °C

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

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

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

Since condensation releases ΔH_{vap} to the surroundings, $\Delta S_{\mathrm{sur}} > 0$

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

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steam → water at 94 °C

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 → water at 94 °C

How to get ΔS_{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 ...

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

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steam → water at 94 °C

For other temperatures ...

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

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[TP] For steam → water

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

At $T = 100$ °C, ΔS_{tot} evaluates to ...

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

BOSTON UNIVERSITY Response Counter 10 10

[TP] For steam → water

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

At $T = 106$ °C, ΔS_{tot} evaluates to …

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

Response Counter

10

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 $\Delta S_{sur} > 0$

The separate roles of ΔS_{sys} and ΔS_{sur} account for 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?

Δ*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?

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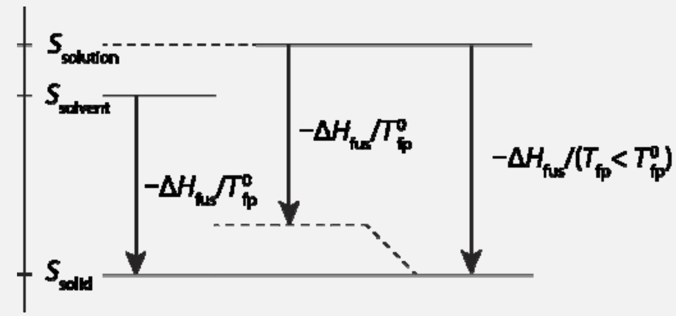
Δ*S* and freezing point depression



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Δ*S* 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-2018/handouts.html

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Absolute entropy, *S*°: The third law of thermodynamics

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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.

$\Delta S_{sys} = \Delta H_{sys}/T_{transition}$

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

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 due to 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.

How to determine $\Delta_r S^o$?

At 0 K, for each substance, $W = 1$ and so $S = 0$.

This is known as the third law of thermodynamics.

Starting for $S(\text{at } T = 0) = 0$, adding a little heat dq, entropy $dS = dq/{\sim}0K$ will be added, raising T a little bit, say to 1 K.

Adding a little more heat dq, entropy $dS = dq/{\sim}1K$ will be added, raising T a little bit, say to 2 K.

Continuing in this way, up to a final temperature T, the sum of all of the small additions dS are S for the substance at T.

These values S are called absolute entropies.