

[TP] The change $W_e(9, 4) \rightarrow W_e(10, 4)$ is $286 - 220 = 66$,
and the change $W_e(4, 4) \rightarrow W_e(5, 4)$ is $56 - 35 = 21$.
For which change do you expect the entropy increase to be greater?

50% 1. $W_e(9, 4) \rightarrow W_e(10, 4)$
50% 2. $W_e(4, 4) \rightarrow W_e(5, 4)$

Lecture 29 CH102 A1 (MWF 9:05 am)

Friday, April 6, 2018

- Heat (energy) flow → entropy change.
- Spontaneity of phase transitions: water ⇌ steam.

Next lecture: ΔS in colligative properties: Freezing point depression. Absolute entropy. Entropy change of reaction

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

Heat (energy) flow → entropy change

Adding energy increases energy dispersal, $W_e(q, m)$.

This means that adding energy increases S.

How does ΔS depend on the energy initially present (q)?

How does ΔS depend on the energy added (Δq)?

ΔS versus energy initially present (q)

Which energy change $(q, m) \rightarrow (q + 1, m)$ has larger ΔS ...

adding 1 quantum to 4: $(4, m) \rightarrow (5, m)$ or ...
adding 1 quantum to 9: $(9, m) \rightarrow (10, m)$?

We can answer theses questions using by analyzing energy dispersal and the corresponding entropy change.

[TP] The change $W_e(9, 4) \rightarrow W_e(10, 4)$ is $286 - 220 = 66$,
and the change $W_e(4, 4) \rightarrow W_e(5, 4)$ is $56 - 35 = 21$.
For which change do you expect the entropy increase to be greater?

50% 1. $W_e(9, 4) \rightarrow W_e(10, 4)$
50% 2. $W_e(4, 4) \rightarrow W_e(5, 4)$

[TP] The general expression for the entropy change of a 4-molecule system with q quanta gaining 1 quantum is ...

25% 1. $W_e(q + 1,4) - W_e(q, 4)$
25% 2. $\ln[W_e(q + 1,4)] - \ln[W_e(q, 4)]$
25% 3. $\ln[W_e(q + 1,4)/W_e(q, 4)]$
25% 4. Both 2 and 3

[TP] Which is larger? (Speeds the evaluations by simplifying ratios.)

0% 1. $W_e(10,4)/W_e(9,4)$
0% 2. $W_e(5,4)/W_e(4,4)$
0% 3. They are equal
0% 4. More information is needed

ΔS versus energy initially present (q)

Which change $(q, m) \rightarrow (q + 1, m)$ has larger ΔS,

adding 1 to 5: $(4, m) \rightarrow (5, m)$ or ...
adding 1 to 9: $(9, m) \rightarrow (10, m)$?

$(4, m) \rightarrow (5, m)$ has larger ΔS than $(9, m) \rightarrow (10, m)$

For a given energy change, ΔS is larger, the less energy (q) initially present.

ΔS is larger, the lower T

Heat (energy) flow → entropy change

For a given energy change, ΔS is larger, the less energy (q) initially present.

What about is ΔS for a given energy (q) initially present?

BOSTON UNIVERSITY 13

[TP] Which is larger? (Simplifying ratios speeds the evaluations.)

1. $W_e(6,4)/W_e(4,4)$
2. $W_e(5,4)/W_e(4,4)$
3. They are equal
4. More information is needed

BOSTON UNIVERSITY 0 of 0 10 14

ΔS versus the energy added (Δq)

Which change $(q, m) \rightarrow (q+1, m)$ or $(q+2, m)$ has larger ΔS,

adding 1 to 4: $(4, m) \rightarrow (5, m)$ or ...

adding 2 to 4: $(4, m) \rightarrow (6, m)$?

$(4, m) \rightarrow (6, m)$ has larger ΔS than $(4, m) \rightarrow (5, m)$

For a given energy (q) initially present , ΔS is larger the larger the energy change.

ΔS is larger, the greater ΔH

BOSTON UNIVERSITY 15

Heat (energy) flow → entropy change

Which changes have larger ΔS?

$(4, m) \rightarrow (5, m)$ has larger ΔS than $(9, m) \rightarrow (10, m)$; $\Delta S \propto 1/T$

$(4, m) \rightarrow (6, m)$ has larger ΔS than $(4, m) \rightarrow (5, m)$; $\Delta S \propto \Delta H$

Taken together, these results illustrate that ...

BOSTON UNIVERSITY 16

Heat (energy) flow → entropy change

ΔS is larger the lower T

ΔS larger the greater ΔH

$\Delta S = \Delta H / T$

Spontaneity of phase transitions

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.

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

14% 1. $\Delta S_{\text{tot}} < 0$
14% 2. $\Delta S_{\text{tot}} = 0$
14% 3. $\Delta S_{\text{tot}} > 0$
14% 4. $\Delta S_{\text{sys}} < 0$ and $\Delta S_{\text{sur}} < 0$
14% 5. $\Delta S_{\text{sys}} < 0$ and $\Delta S_{\text{sur}} = 0$
14% 6. $\Delta S_{\text{sys}} < 0$ and $\Delta S_{\text{sur}} > 0$
14% 7. None of the above

steam → water at 94 °C

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

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

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

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

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

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

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

steam → 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} ...

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