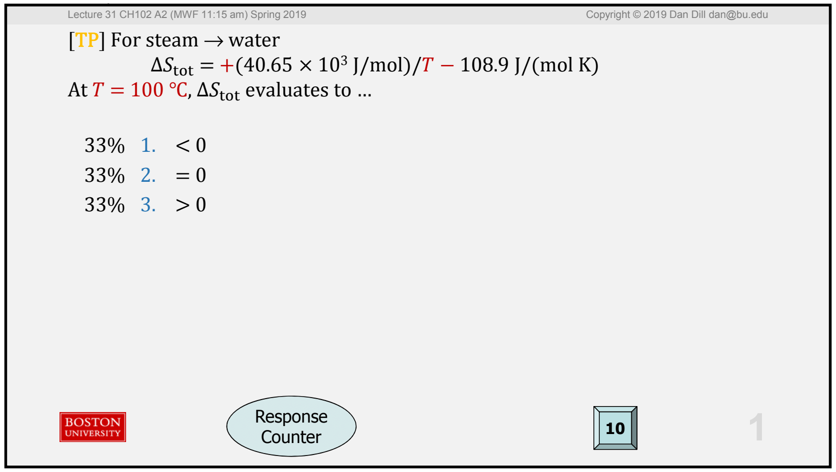


[TP] For steam → water

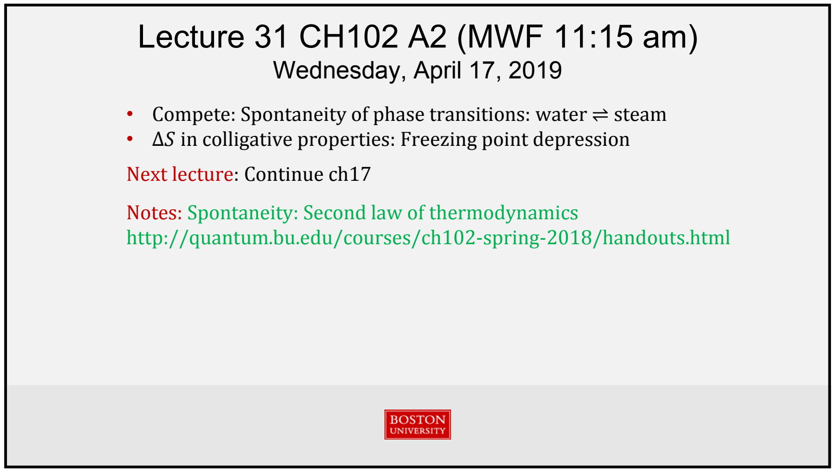
$$\Delta S_{\text{tot}} = +(40.65 \times 10^3\ \text{J/mol})/T - 108.9\ \text{J/(mol K)}$$

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

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

Response Counter

10



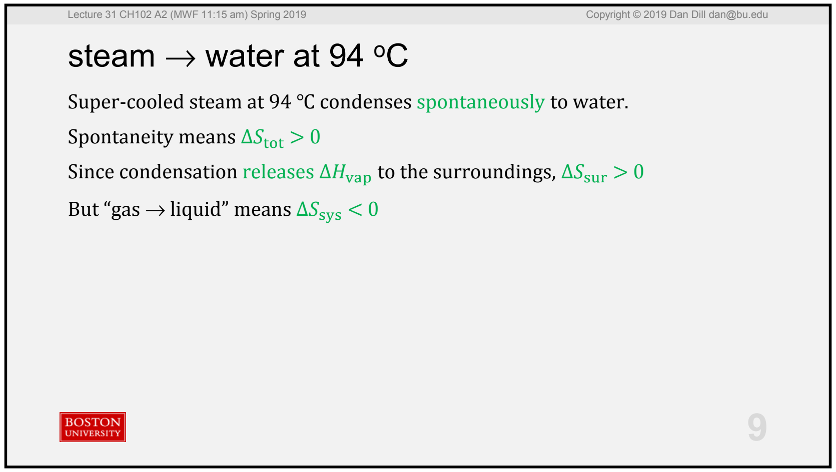
Lecture 31 CH102 A2 (MWF 11:15 am)

Wednesday, April 17, 2019

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

Next lecture: Continue ch17

Notes: Spontaneity: Second law of thermodynamics
http://quantum.bu.edu/courses/ch102-spring-2018/handouts.html



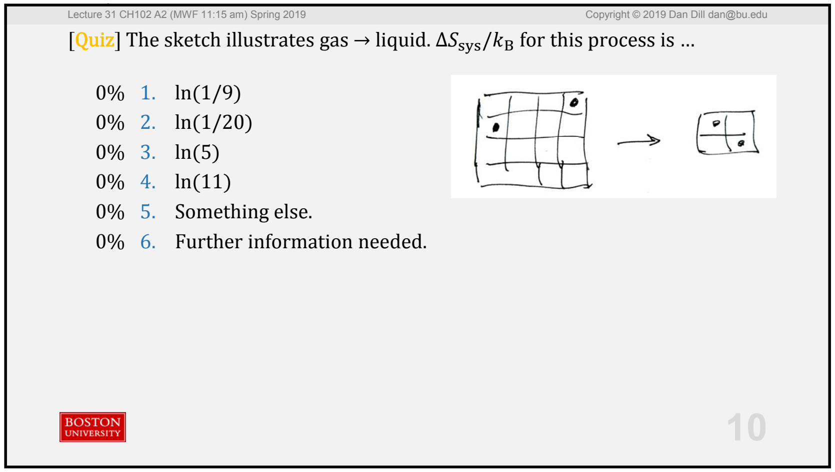
steam → water at 94 °C

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

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

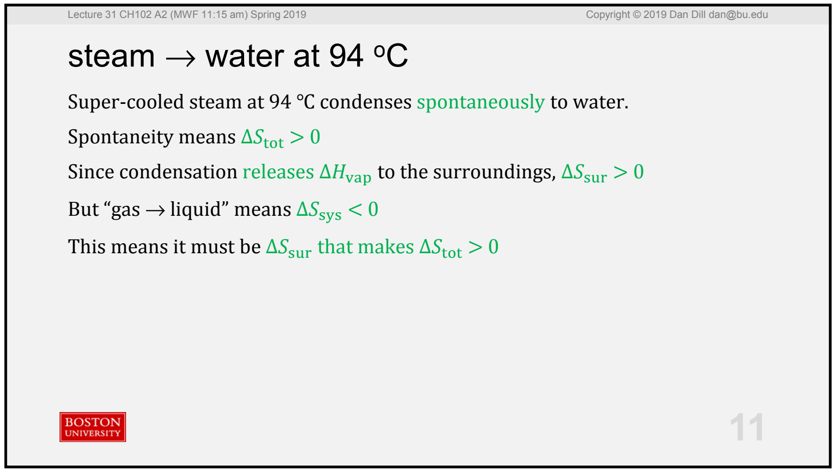
Since condensation releases ΔH_{vap} to the surroundings, $\Delta S_{\text{sur}} > 0$

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



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

0% 1. ln(1/9)
0% 2. ln(1/20)
0% 3. ln(5)
0% 4. ln(11)
0% 5. Something else.
0% 6. Further information needed.



steam → water at 94 °C

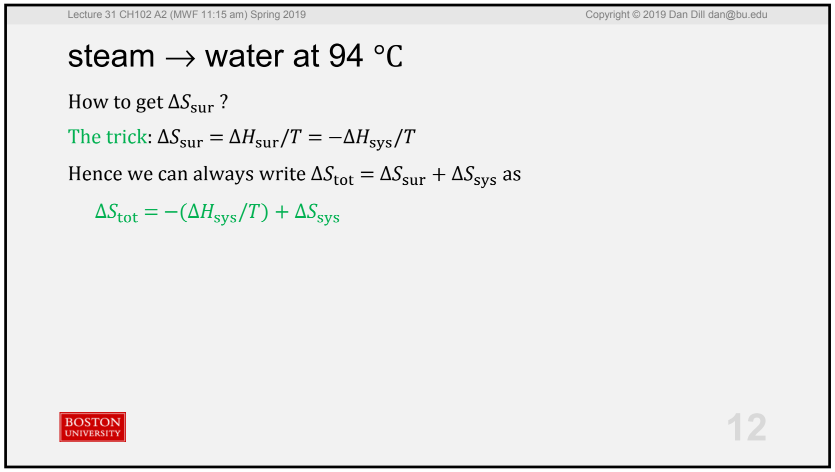
Super-cooled steam at 94 °C condenses spontaneously to water.

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



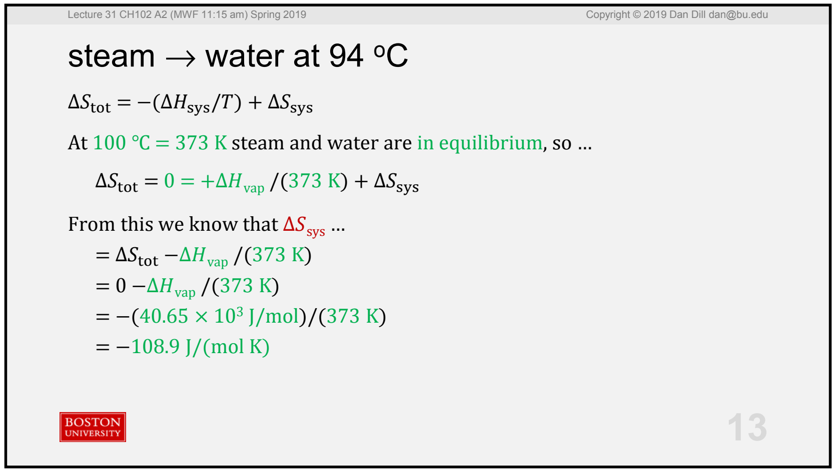
steam → water at 94 °C

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

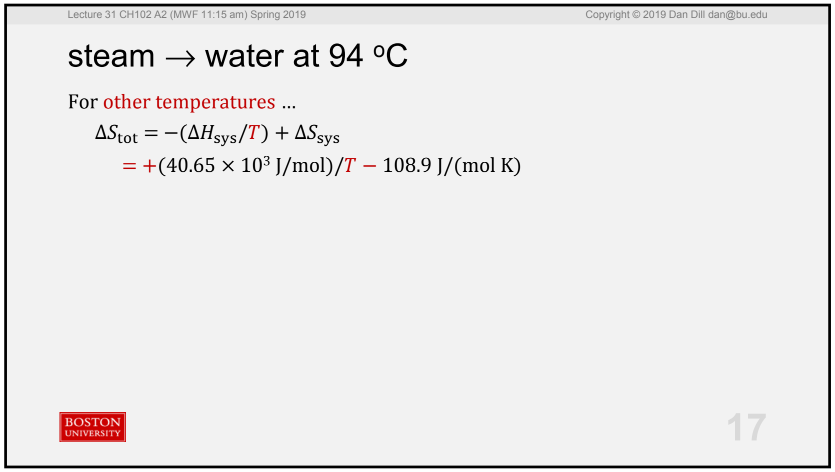
$\Delta S_{\text{tot}} = -(\Delta H_{\text{sys}}/T) + \Delta S_{\text{sys}}$

At 100 °C = 373 K 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} …

$$= \Delta S_{\text{tot}} - \Delta H_{\text{vap}}/(373\ \text{K})$$
$$= 0 - \Delta H_{\text{vap}}/(373\ \text{K})$$
$$= -(40.65 \times 10^3\ \text{J/mol})/(373\ \text{K})$$
$$= -108.9\ \text{J/(mol K)}$$



steam → water at 94 °C

For other temperatures …

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

[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

[TP] For steam → water

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

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

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

Response Counter

10

Taking stock

Spontaneity means that ...

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

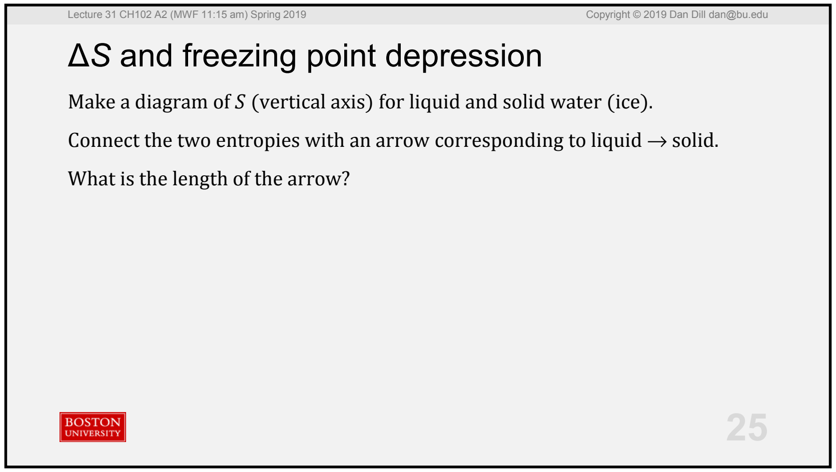
Spontaneity does not require that ...

$\Delta S_{\text{sys}} > 0$ or $\Delta S_{\text{sur}} > 0$

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

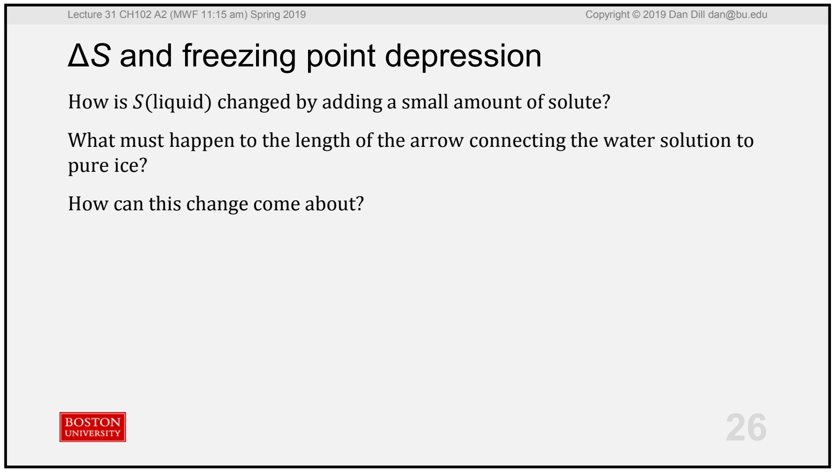


ΔS and freezing point depression

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?

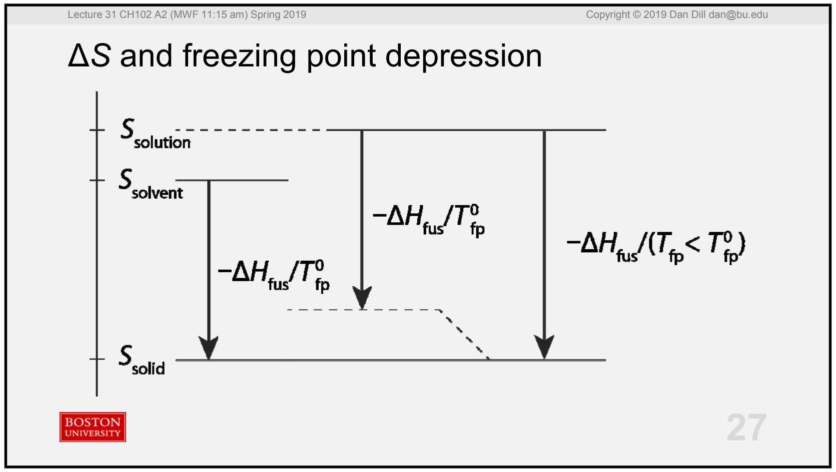


ΔS and freezing point depression

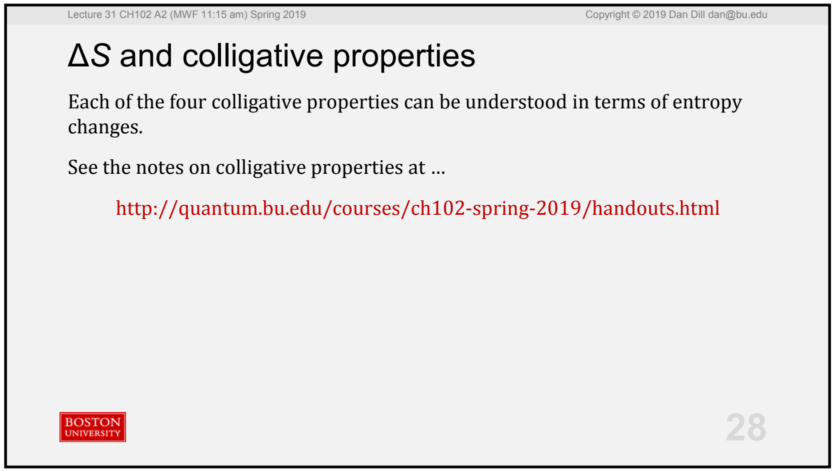
How is S(liquid) changed by adding a small amount of solute?

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



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-2019/handouts.html