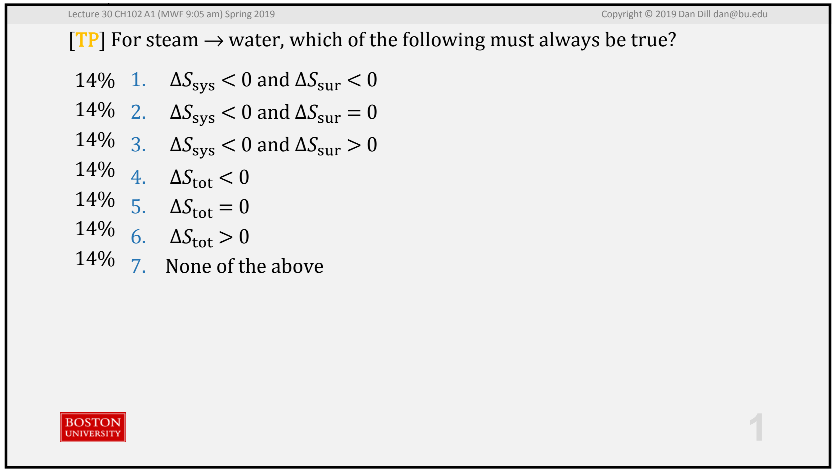
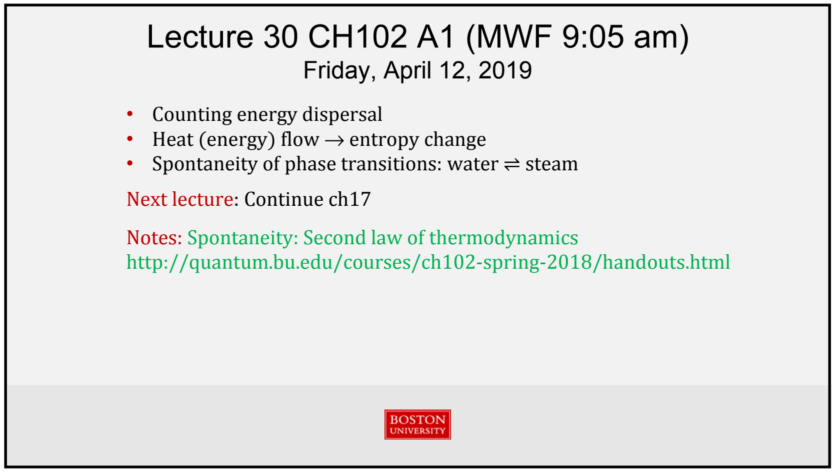


[TP] For steam → water, which of the following must always be true?

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

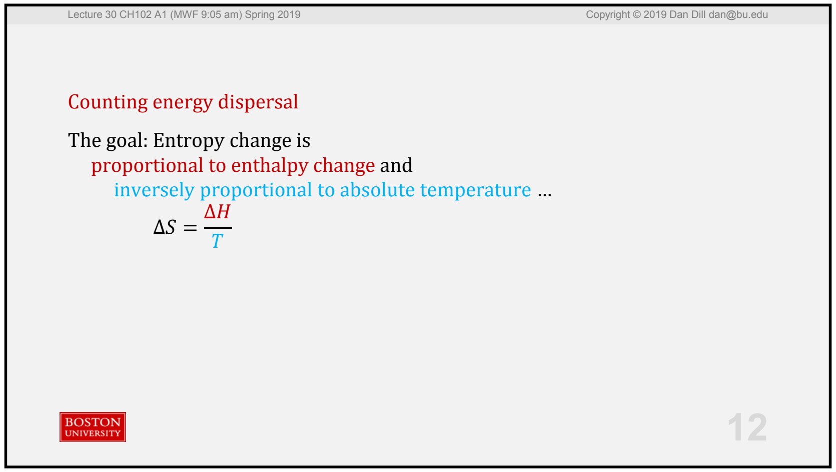

Lecture 30 CH102 A1 (MWF 9:05 am)

Friday, April 12, 2019

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

Next lecture: Continue ch17

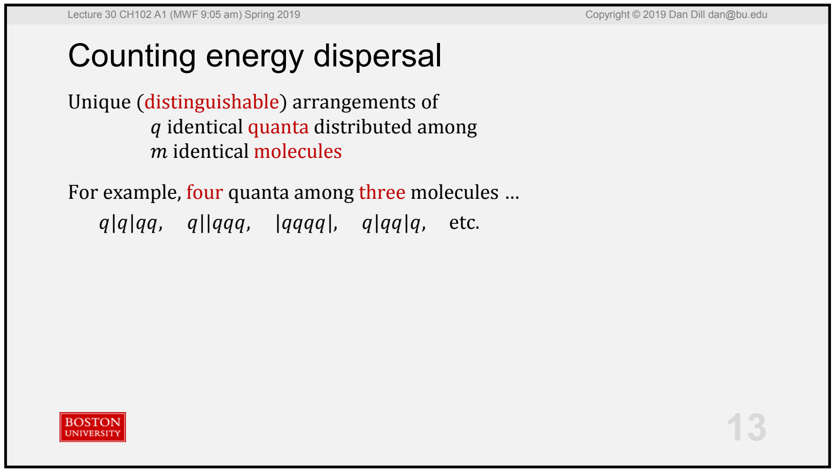
Notes: Spontaneity: Second law of thermodynamics
http://quantum.bu.edu/courses/ch102-spring-2018/handouts.html



Counting energy dispersal

The goal: Entropy change is
proportional to enthalpy change and
inversely proportional to absolute temperature …

$$\Delta S = \frac{\Delta H}{T}$$

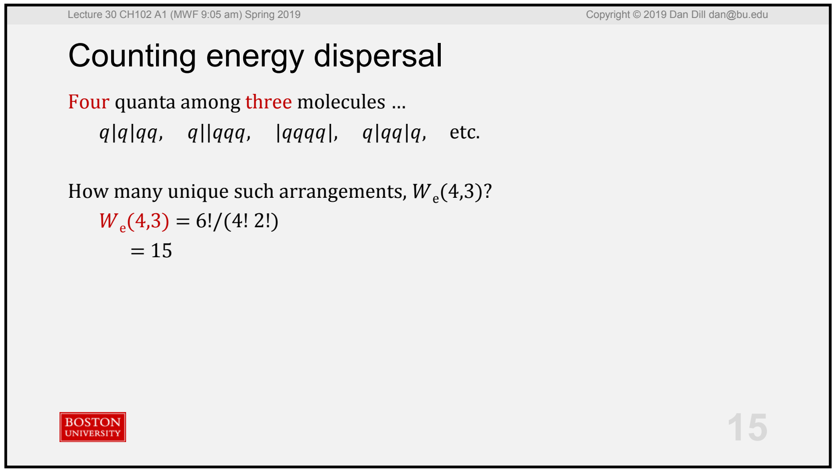


Counting energy dispersal

Unique (distinguishable) arrangements of
q identical quanta distributed among
m identical molecules

For example, four quanta among three molecules …

$q|q|qq$, $q||qqq$, $|qqqq|$, $q|qq|q$, etc.



Counting energy dispersal

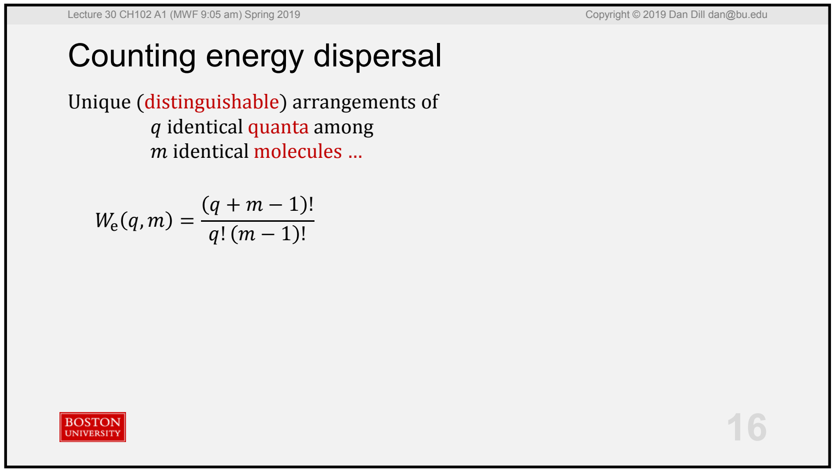
Four quanta among three molecules ...

$q|q|qq$, $q||qqq$, $|qqqq|$, $q|qq|q$, etc.

How many unique such arrangements, $W_e(4,3)$?

$W_e(4,3) = 6!/(4!\,2!)$

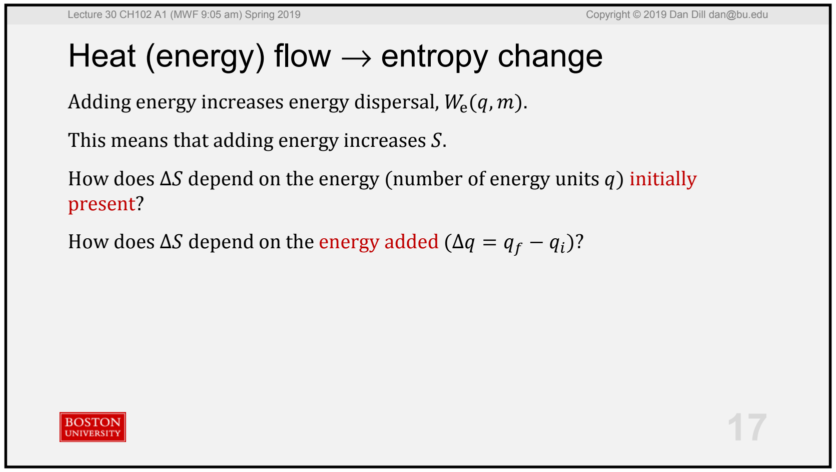
$= 15$



Counting energy dispersal

Unique (distinguishable) arrangements of
q identical quanta among
m identical molecules ...

$$W_e(q,m) = \frac{(q+m-1)!}{q!\,(m-1)!}$$



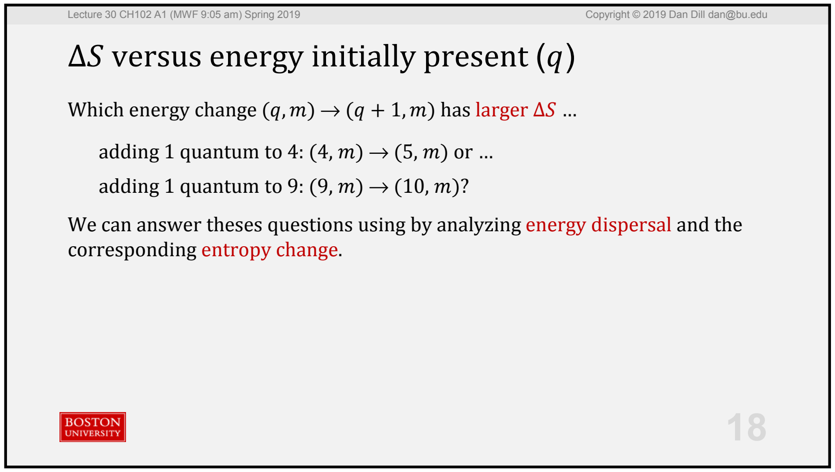
Heat (energy) flow → entropy change

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

This means that adding energy increases S.

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

How does ΔS depend on the energy added ($\Delta q = q_f - q_i$)?



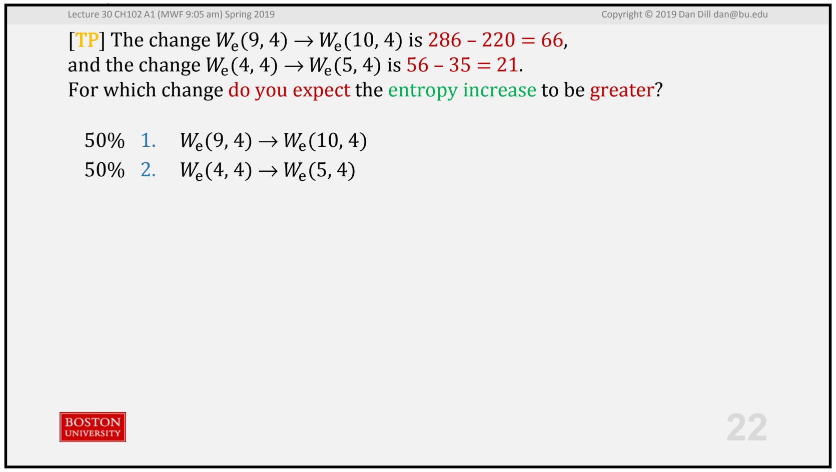
ΔS versus energy initially present (q)

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

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

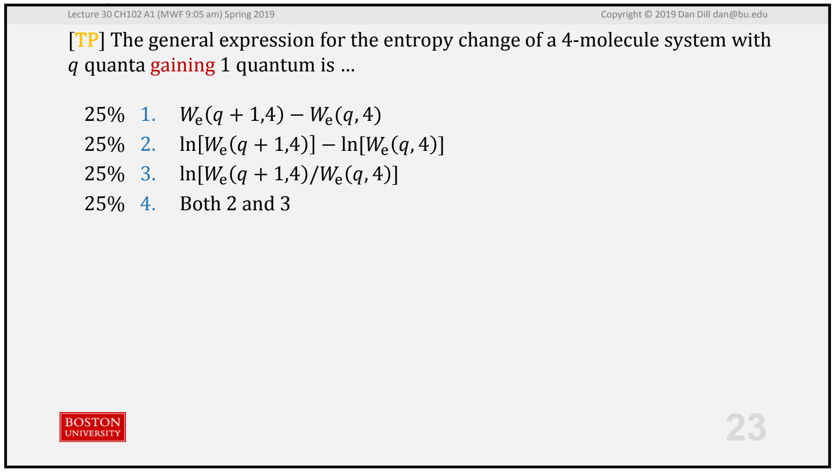
adding 1 quantum to 9: $(9,m) \to (10,m)$?

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



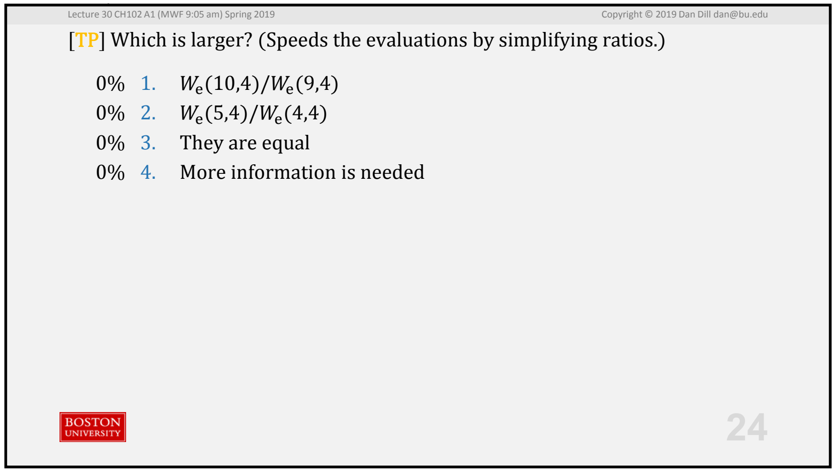
[TP] The change $W_e(9, 4) \to W_e(10, 4)$ is $286 - 220 = 66$, and the change $W_e(4, 4) \to W_e(5, 4)$ is $56 - 35 = 21$. For which change do you expect the entropy increase to be greater?

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



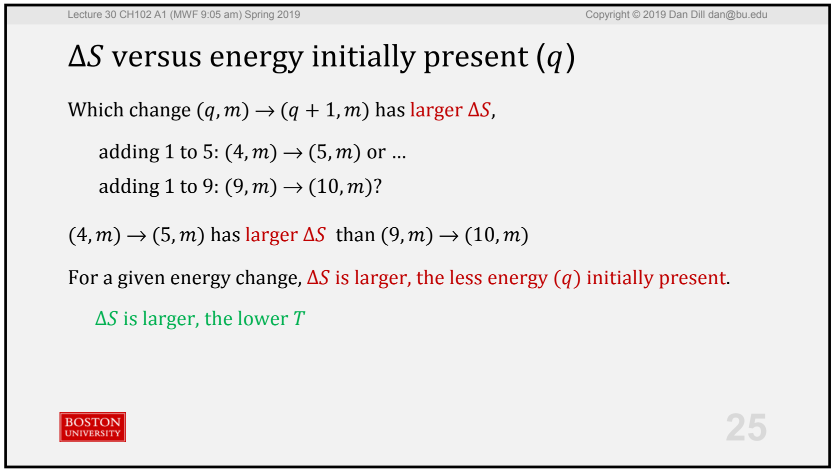
[TP] The general expression for the entropy change of a 4-molecule system with q quanta gaining 1 quantum is …

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)

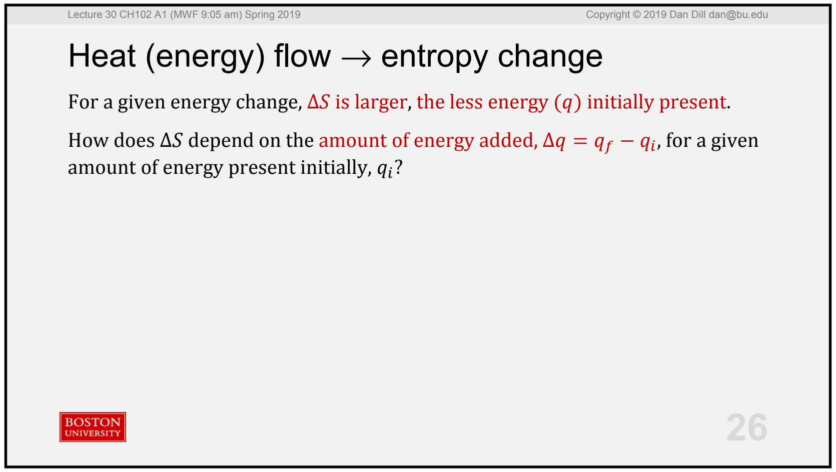
Which change $(q, m) \to (q + 1, m)$ has larger ΔS,

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

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

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

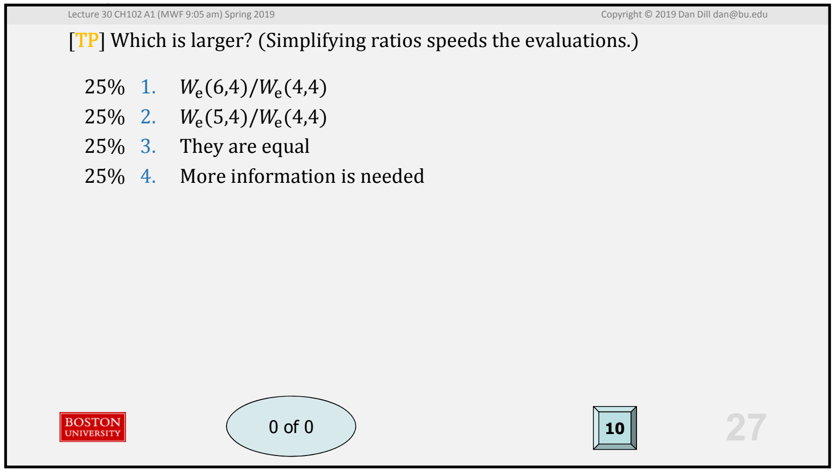
ΔS is larger, the lower T



Heat (energy) flow → entropy change

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

How does ΔS depend on the amount of energy added, $\Delta q = q_f - q_i$, for a given amount of energy present initially, q_i?

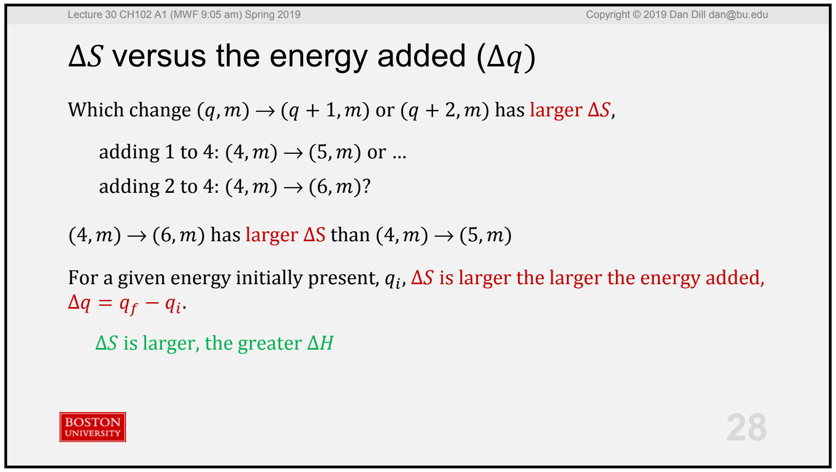


[TP] Which is larger? (Simplifying ratios speeds the evaluations.)

25% 1. $W_e(6,4)/W_e(4,4)$
25% 2. $W_e(5,4)/W_e(4,4)$
25% 3. They are equal
25% 4. More information is needed

0 of 0

10



ΔS versus the energy added (Δq)

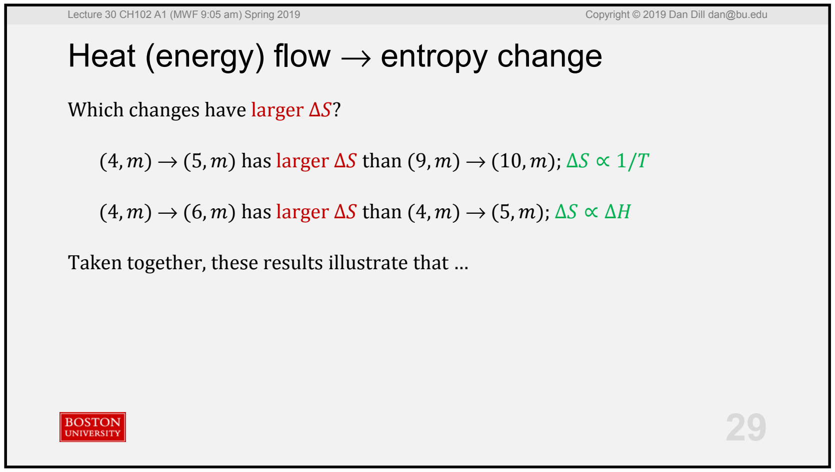
Which change $(q, m) \to (q+1, m)$ or $(q+2, m)$ has larger ΔS,

adding 1 to 4: $(4, m) \to (5, m)$ or …
adding 2 to 4: $(4, m) \to (6, m)$?

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

For a given energy initially present, q_i, ΔS is larger the larger the energy added, $\Delta q = q_f - q_i$.

ΔS is larger, the greater ΔH



Heat (energy) flow → entropy change

Which changes have larger ΔS?

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

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

Taken together, these results illustrate that …

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 ...

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

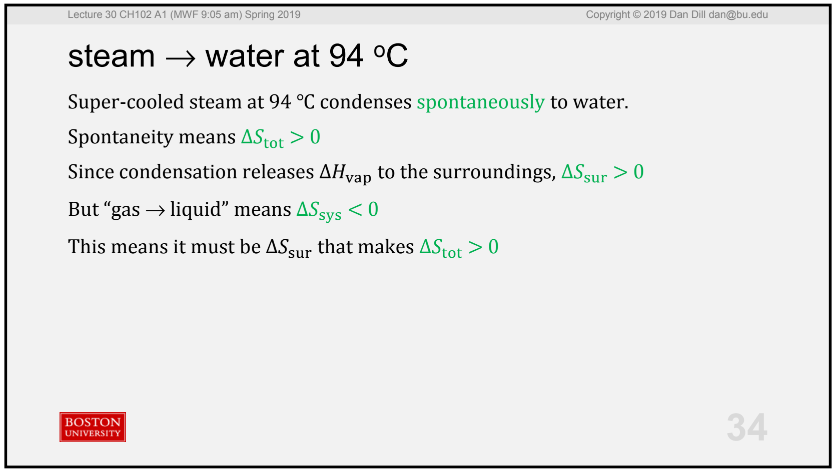
Spontaneity does not require that ...

$\Delta S_{\text{sys}} > 0$ 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. $\Delta S_{\text{sys}} < 0$ and $\Delta S_{\text{sur}} < 0$
14% 2. $\Delta S_{\text{sys}} < 0$ and $\Delta S_{\text{sur}} = 0$
14% 3. $\Delta S_{\text{sys}} < 0$ and $\Delta S_{\text{sur}} > 0$
14% 4. $\Delta S_{\text{tot}} < 0$
14% 5. $\Delta S_{\text{tot}} = 0$
14% 6. $\Delta S_{\text{tot}} > 0$
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 $\Delta S_{\text{tot}} > 0$