Lecture 20 CH102 A3 (TuTh 5 pm)

Tuesday, April 5, 2016

For today ...

- Continue Ch. 17 Spontaneous change – how far?
  - Heat flow and entropy change
  - Spontaneity of phase transitions
  - The role of ΔS in colligative properties

Next lecture:

- Continue Ch. 17 Spontaneous change – how far?
  - Entropy change for chemical reactions

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Heat (energy) flow [?] entropy change

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

Which energy change (q, m) [?] $(q + 1, m)$ has larger ΔS ...

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

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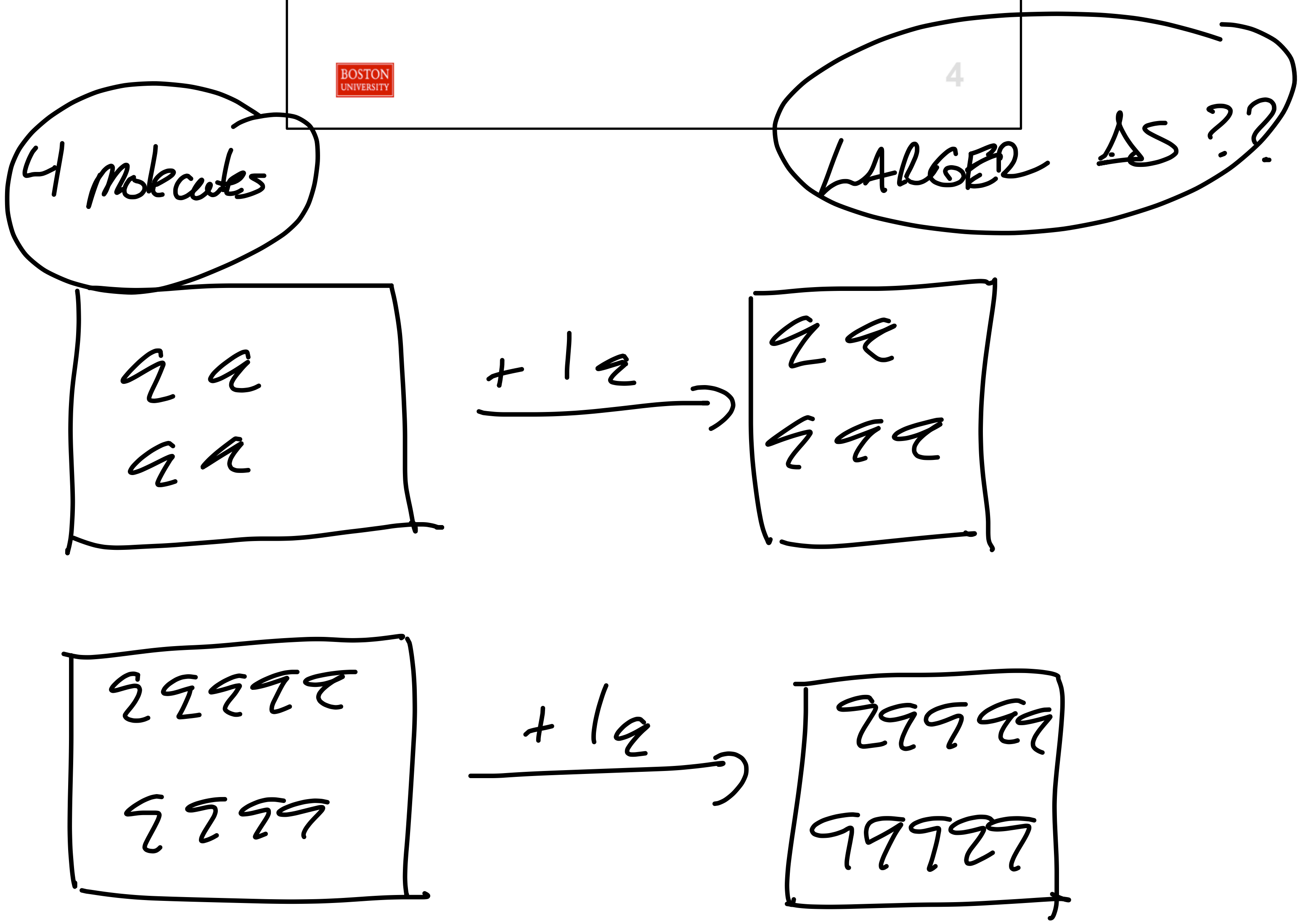

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[TP] Evaluate W_e(4 quanta, 4 molecules).

25%	1.	14 x 5 = 70
25%	2.	7 x 5 = 35
25%	3.	4 x 5 = 20
25%	4.	None of the above

$$W_e(4,4) = \frac{(4+(4-1))!}{4!\,(4-1)!} = \frac{7!}{4!\,3!} = \frac{7\times 6\times 5}{3\cdot 2} = 35$$

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$$W_e(5,4) = \frac{(5+3)!}{5!\,3!} = \frac{8\cdot 7\cdot 6}{6} = 56$$

[TP] Evaluate W_e(9 quanta, 4 molecules).

25% 1. 11 x 10 = 110

25% 2. 10 x 22 = 220

25% 3. 13 x 11 = 143

25% 4. None of the above

$$W_e(9,4) = \frac{(9+3)!}{9!\,3!} = \frac{12 \cdot 11 \cdot 10}{3 \cdot 2}$$

$$= 22 \cdot 10 = 220$$

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[TP] Evaluate W_e(10 quanta, 4 molecules).

25% 1. 13 x 12 x 11 = 1716
25% 2. 12 x 11 = 132
25% 3. 13 x 2 x 11 = 286
25% 4. None of the above

$$W_e(10,4) = \frac{(10+3)!}{10!\,3!} = \frac{13\cdot 12\cdot 11}{6}$$

$$= 13\cdot 2\cdot 11 = 286$$

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[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

$$S = k_B \ln W$$

$$\Delta S = k_B \ln\left(\frac{W_f}{W_i}\right) = k_B [\ln W_f - \ln W_i]$$

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$$W_f = W_e(q+1, 4)$$
$$W_i = W_e(q, 4)$$

[TP] Which is larger?

33% 1. $W_e(10, 4) / W_e(9, 4)$
33% 2. $W_e(5, 4) / W_e(4, 4)$
33% 3. More information is needed

$$\frac{W_e(10,4)}{W_e(9,4)} = \frac{286}{220} = 1.3$$

$$\frac{W_e(5,4)}{W_e(4,4)} = \frac{56}{35} = 1.6$$

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$$W_e(5,4) = \frac{(5+3)!}{5!\,3!} = \frac{8!}{5!\,3!} = \frac{8 \cdot 7 \cdot 6}{6} = 56$$

Heat (energy) flow ? entropy change

Which change (q, m) ? (q + 1, m) has larger ΔS,

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

(4, m) ? (5, m) has *larger* ΔS than (9, m) ? (10, m)

This result illustrates that …

ΔS is larger, the lower T

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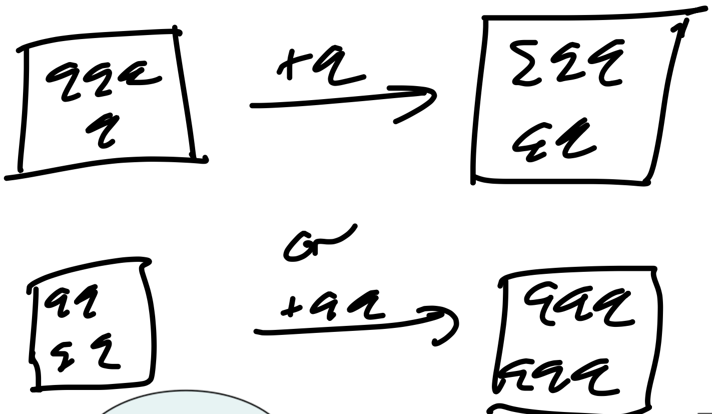
[TP] Which is larger?

33% 1. $W_e(6, 4) / W_e(4, 4)$

33% 2. $W_e(5, 4) / W_e(4, 4)$

33% 3. More information is needed



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Heat (energy) flow ? entropy change

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

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

$(4, m)$? $(6, m)$ has *larger* ΔS than $(4, m)$? $(5, m)$

This result illustrates that …

ΔS larger, the greater ΔH

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Heat (energy) flow ? entropy change

Which changes have larger ΔS?

(4, m) ? (5, m) has *larger* ΔS than (9, m) ? (10, m)

(4, m) ? (6, m) has *larger* ΔS than (4, m) ? (5, m)

These results illustrate that ...

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

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$$\Delta S \propto \frac{1}{T}$$

$$\Delta S \propto \Delta H$$

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

Spontaneity of phase transitions

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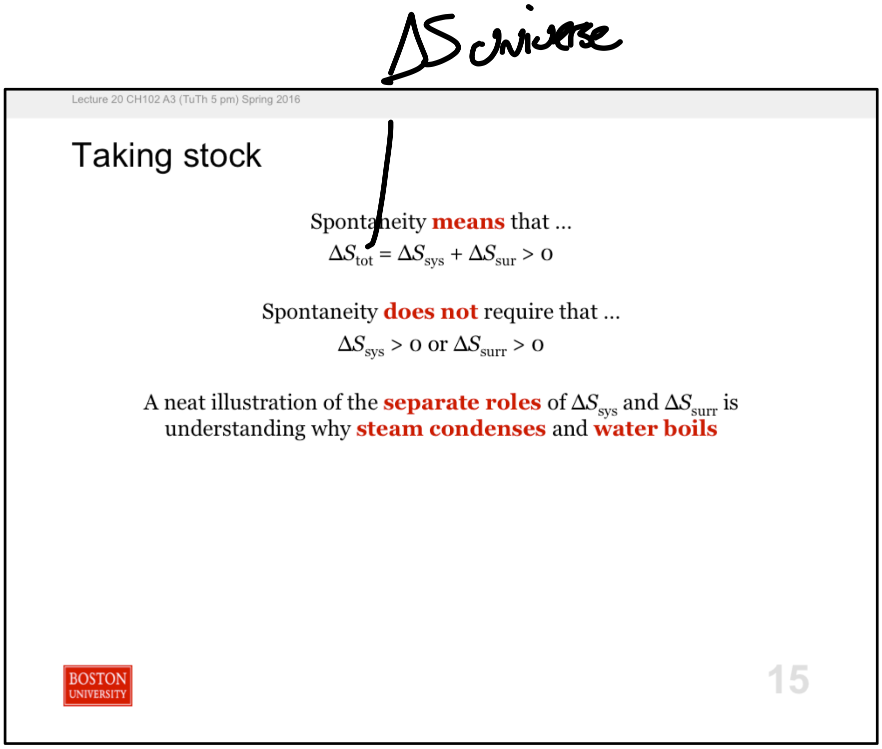
ΔS universe
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Taking stock
Spontaneity **means** that ...
$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{sur} > 0$
Spontaneity **does not** require that ...
$\Delta S_{sys} > 0$ or $\Delta S_{surr} > 0$
A neat illustration of the **separate roles** of ΔS_{sys} and ΔS_{surr} is understanding why **steam condenses** and **water boils**
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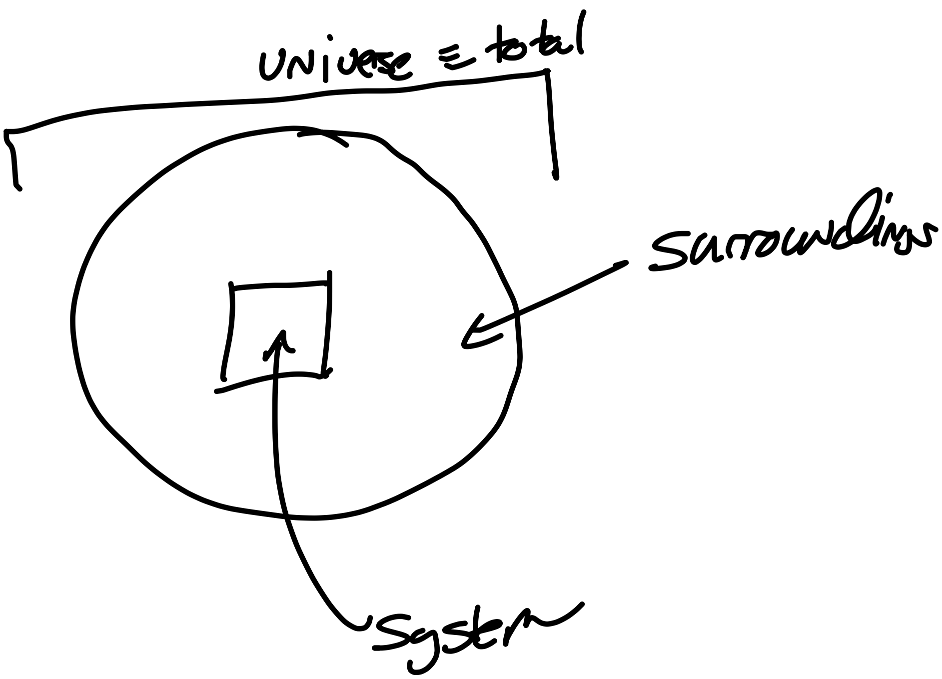
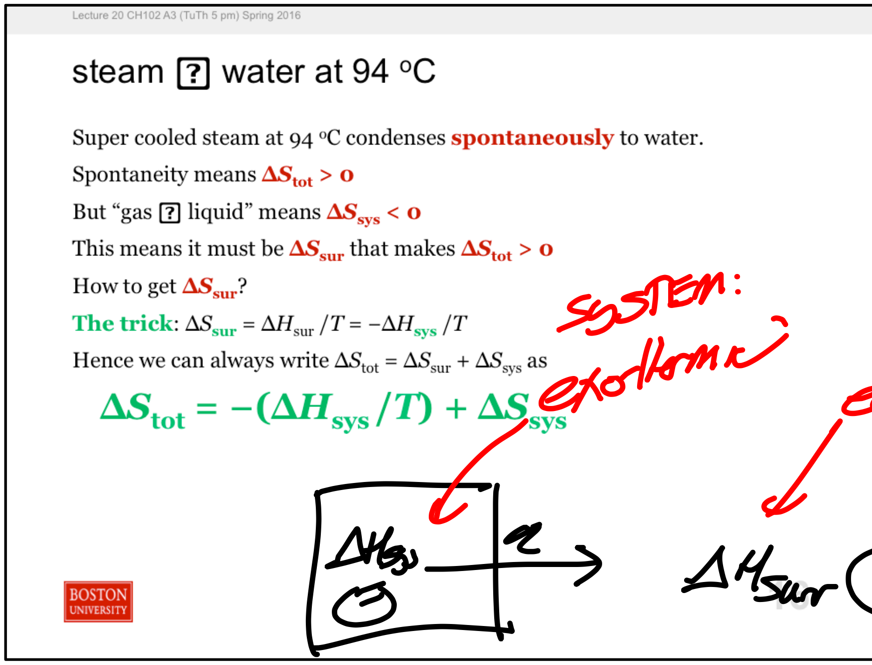
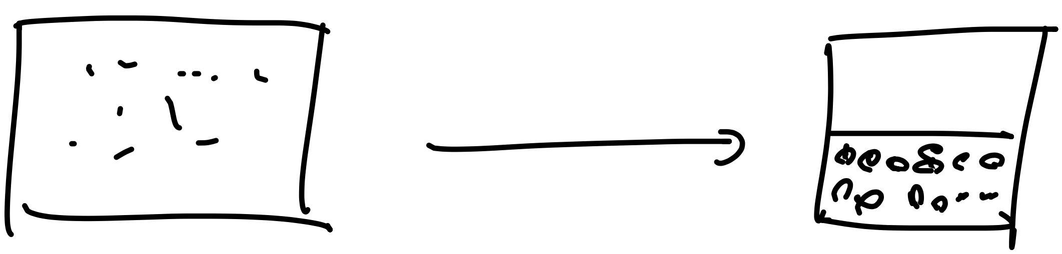

universe = total
surroundings
system

$$\Delta S_{sur} = \frac{\Delta H_{sur}}{T}$$

where does this come from? heat transfer to or from system!





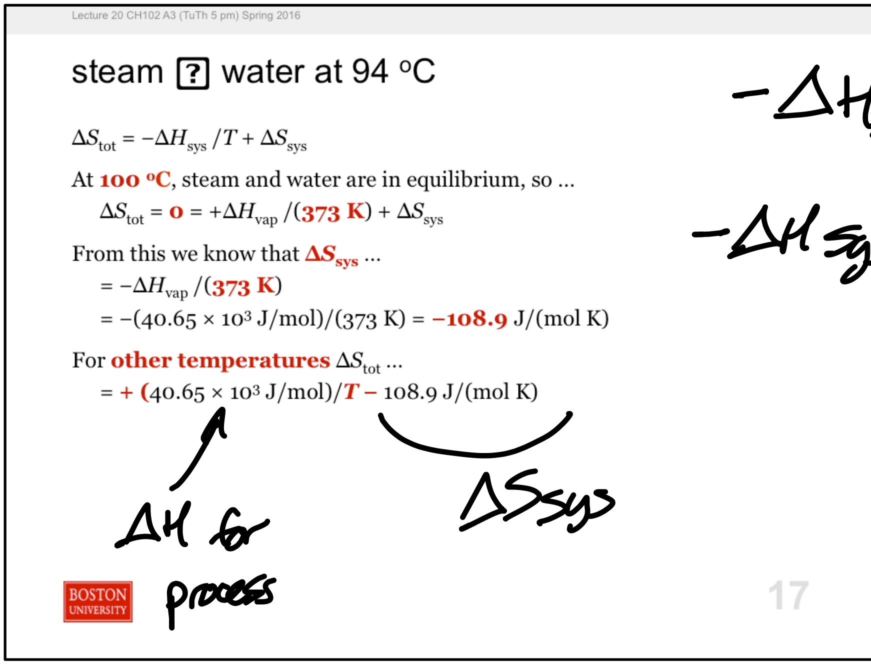
gas: lots of arrangements → liquid: fewer arrangements

$\Delta S = (-)$

$$\underset{(+)}{\Delta S_{tot}} = \underset{(-)}{\Delta S_{sys}} + \underset{(+)}{\Delta S_{sur}}$$

must be!!

ΔH_{sys} = "$\Delta H_{CONDENSATION}$" = $-\Delta H_{VAP}$ (⊖ over $\Delta H_{CONDENSATION}$, ⊕ over ΔH_{VAP})



$-\Delta H_{sys} = -(-\Delta H_{vap})$

$-\Delta H_{sys} = +\Delta H_{vap}$

ΔH_{vap} : l → g

endothermic process ΔH ⊕
(add heat)

CONDENSATION: g → l

exothermic process ΔH ⊖
(gives off heat)

[TP] For steam [?] water

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

At $T = 94$ °C , ΔS_{tot} evaluates to ...

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

At 100 °C, $\Delta S_{tot} = 0$

At < 100 °C, T smaller, so first term bigger, $\Delta S = (+)$

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spontaneous –

yes, STEAM condenses below 100 °C !

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[TP] For steam ? water

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

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

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

100 °C is the equilibrium temperature!

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$\Delta S_{total} > 0$ SPONTANEOUS

$\Delta S_{total} = 0$ equilibrium

$\Delta S_{total} < 0$ not spontaneous

[Quiz] For steam [?] water

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

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

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

CONDENSATION OF STEAM IS NOT SPONTANEOUS AT TEMPERATURE >100 °C !

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