Lecture 12 CH131 Summer 1

Tuesday, June 11, 2019

- Complete: Arrangements → entropy
- Heat (energy) flow → entropy change
- Entropy change of reaction
- System-only measure of spontaneity: ΔG
- Example problems

Next lecture: Complete ch13. Begin ch14 Continue ch14

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ΔS for osmotic pressure

xoxxoo | xooyoy → xoooxo | xyoyxo

Spontaneous?

Calculate the entropy change

$W_i = W_p(3,3) \times W_p(3,2,1) \rightarrow W_f = W_p(4,2) \times W_p(2,2,2)$

1200 → 1350

$\Delta S = S_f - S_i = k_B \ln(\underset{>1}{W_f/W_i})$

$\ln(W_f/W_i) = \ln(1350/1200) = 0.118 \cancel{>1} > 0$

$W_f/W_i > 1$ so

$\ln(W_f/W_i) > 0$

$\Delta S = S_f - S_i = + 0.118\ k_B$ (spontaneous!)

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Heat (energy) flow → entropy change

Adding energy increases energy dispersal (W_e, the arrangements of energy).

This means that adding energy increases entropy, $S = k_B \ln(\underset{\varepsilon}{W_e})$.

Does the entropy increase depend on how much energy is initially present?

How does ΔS_1 for adding 10 J to 1 mol at 300 K compare with ΔS_2 for adding 10 J to 1 mol at 600 K?

$\boxed{\Delta S_1 > \Delta S_2}$

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Heat (energy) flow → entropy change

Adding energy increases energy dispersal (W_e, the arrangements of energy).

This means that adding energy increases entropy, $S = k_B \ln(W_e)$.

Is entropy increase greater the more energy added ~~originally present~~?

How does ΔS_1 for adding 10 J to 1 mol at 300 K compare with ΔS_3 for adding 20 J to 1 mol at 300 K?

$\Delta S_1 < \Delta S_3$

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Heat (energy) flow → entropy change

$\frac{W_f}{W_i}$

ΔS is larger the lower T, the less the energy already present

$\Delta S_1 > \Delta S_2$

ΔS larger the greater ΔH, the more energy that is transferred

$\Delta S_3 > \Delta S_1$

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

$PV = nRT$

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

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How to determine $\Delta S_{\text{sur}} = \Delta H_{\text{sur}} / T$?

$\Delta S_{tot} = \Delta S_{sys} + \boxed{\Delta S_{surr}}$

q, w

T_{surr}

In principle, we can get ΔS_{sys} by analyzing changes in particle and energy dispersal in the system.

But how to get ΔS_{sur}?

W_f, W_c

The key is energy conservation, namely that …

$H_2O(s) \rightarrow H_2O(l)$

$\Delta H_{sys} = \Delta H_{fus}$

$\Delta H_{\text{sur}} = -\Delta H_{\text{sys}}$

So, …

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

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How to determine ΔS_{sys}?

We can get ΔS_{sys} by analyzing changes in particle and energy dispersal in the system.

But, in practice, it is easier to get ΔS_{sys} by measuring heat flow between system and surroundings when they are in equilibrium.

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How to determine $\Delta_r S^o$?

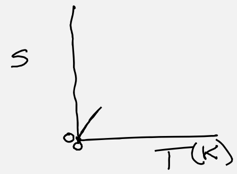
At equilibrium, $\Delta S_{\text{tot}} = 0$, and so …

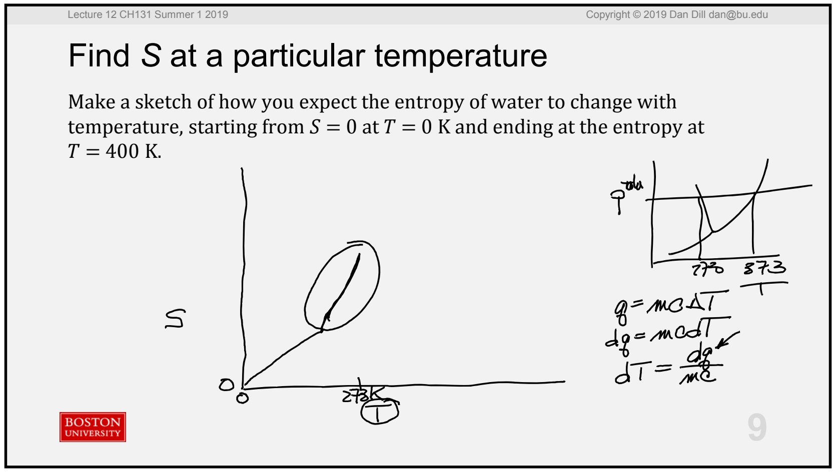
$\Delta S_{\text{sys}} = -\Delta S_{\text{sur}} = -\Delta H_{\text{sur}}/T = +\Delta H_{\text{sys}}/T$

At 0 K, for each substance $\underline{W = 1}$ and so $\underline{S = 0}$! (Third Law)

Therefore, by accumulating changes in S during heating, we can find S at a particular temperature

$+\frac{dq}{T}$





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Find *S* at a particular temperature

Make a sketch of how you expect the entropy of water to change with temperature, starting from $S = 0$ at $T = 0$ K and ending at the entropy at $T = 400$ K.

$q = mc\Delta T$

$dq = mc\,dT$

$dT = \frac{dq}{mc}$

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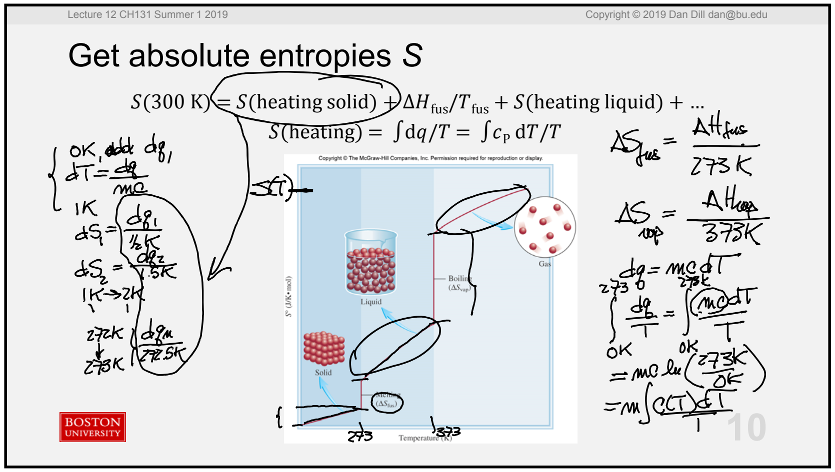

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Get absolute entropies *S*

$S(300\text{ K}) = S(\text{heating solid}) + \Delta H_{\text{fus}}/T_{\text{fus}} + S(\text{heating liquid}) + \ldots$

$S(\text{heating}) = \int dq/T = \int c_P\,dT/T$

0K, add dq_1

$dT = \frac{dq}{mc}$

1K $dS_1 = \frac{dq_1}{\frac{1}{2}K}$

$dS_2 = \frac{dq_2}{1.5K}$

1K→2K

272K → 273K $\frac{dq_m}{272.5K}$

$S(T)$

$\Delta S_{fus} = \frac{\Delta H_{fus}}{273\text{ K}}$

$\Delta S_{vap} = \frac{\Delta H_{vap}}{373\text{K}}$

$dq = mc\,dT$

$\int_{0K}^{273} \frac{dq}{T} = \int_{0K}^{273K} \frac{mc\,dT}{T}$

$= mc \ln\left(\frac{273K}{0K}\right)$

$= m\int \frac{c(T)\,dT}{T}$

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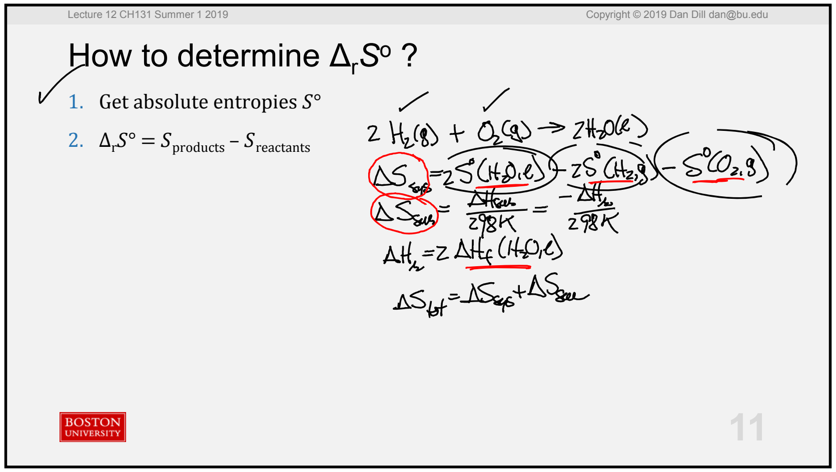

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How to determine $\Delta_r S^o$?

✓

1. Get absolute entropies $S°$
2. $\Delta_r S° = S_{\text{products}} - S_{\text{reactants}}$

✓ ✓

$2\,H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

$\Delta S_{sys} = 2S°(H_2O,l) - 2S°(H_2,g) - S°(O_2,g)$

$\Delta S_{surr} = \frac{\Delta H_{surr}}{298K} = \frac{-\Delta H_{sys}}{298K}$

$\Delta H_{sys} = 2\,\Delta H_f(H_2O,l)$

$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr}$

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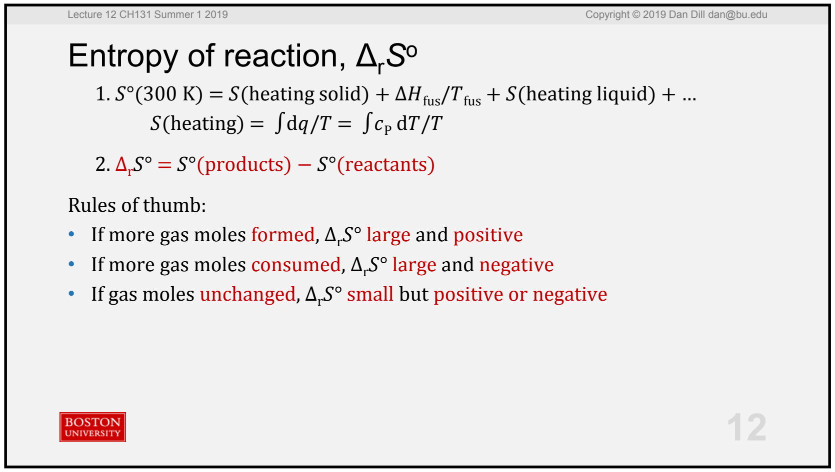

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Entropy of reaction, $\Delta_r S^o$

1. $S°(300\text{ K}) = S(\text{heating solid}) + \Delta H_{\text{fus}}/T_{\text{fus}} + S(\text{heating liquid}) + \ldots$

   $S(\text{heating}) = \int dq/T = \int c_P\,dT/T$

2. $\Delta_r S° = S°(\text{products}) - S°(\text{reactants})$

Rules of thumb:

- If more gas moles formed, $\Delta_r S°$ large and positive
- If more gas moles consumed, $\Delta_r S°$ large and negative
- If gas moles unchanged, $\Delta_r S°$ small but positive or negative

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$\Delta_r S^o$ = S^o(products) − S^o(reactants)

Rules of thumb:

- If more gas moles formed, $\Delta_r S°$ large and positive
- If more gas moles consumed, $\Delta_r S°$ large and negative
- If gas moles unchanged, $\Delta_r S°$ small but positive or negative

$\Delta S_r = 2\,S°(ZnO,s) - 2\,S°(Zn,s) - S°(O_2,g)$

$= -200.8$ J/K

$2\ \underset{2\ mol}{Zn(s)} + O_2(g) \xrightarrow{} 2\ ZnO(s)$ J/K mol

$\Delta_r S° = \textcircled{2} \times 43.7 - (2 \times 41.6 + 205.0) = \boxed{-200.8\ J/K}$

$\Delta n_g = -1$, so $\Delta_r S°$ is large and negative

$\Delta_r S^o$ = S^o(products) − S^o(reactants)

Rules of thumb:

- If more gas moles formed, $\Delta_r S°$ large and positive
- If more gas moles consumed, $\Delta_r S°$ large and negative
- If gas moles unchanged, $\Delta_r S°$ small but positive or negative

$N_2(g) + O_2(g) \rightarrow 2\ NO(g)$

$\Delta_r S° = 2 \times 210.8 - (191.6 + 205.0) = +25$ J/K

$\Delta n_g = 0$, so $\Delta_r S°$ is small

System-only spontaneity measure

Since spontaneity depends on total entropy change, ...

We cannot tell about spontaneity from ΔS_{sys} alone.

We need also to know about ΔS_{sur}.

But since $\Delta S_{sur} = -\Delta H_{sys}/T$ ...

we can express ΔS_{tot} in terms of ...

ΔS_{sys}, ΔH_{sys} and T only.

$$\Delta S_{tot} = \Delta S_{sur} + \Delta S_{sys}$$

$$= -\frac{\Delta H_{sys}}{T} + \Delta S_{sys}$$

$$-T\Delta S_{tot} = +\Delta H_{sys} - T\Delta S_{sys}$$

$$\Delta G =$$

System-only spontaneity measure

$\Downarrow$

$\Delta G \equiv \Delta H_{sys} - T\Delta S_{sys}$

Gibbs free energy change is defined as

$$\Delta G = -T\Delta S_{tot} = -T\Delta S_{sur} - T\Delta S_{sys}$$

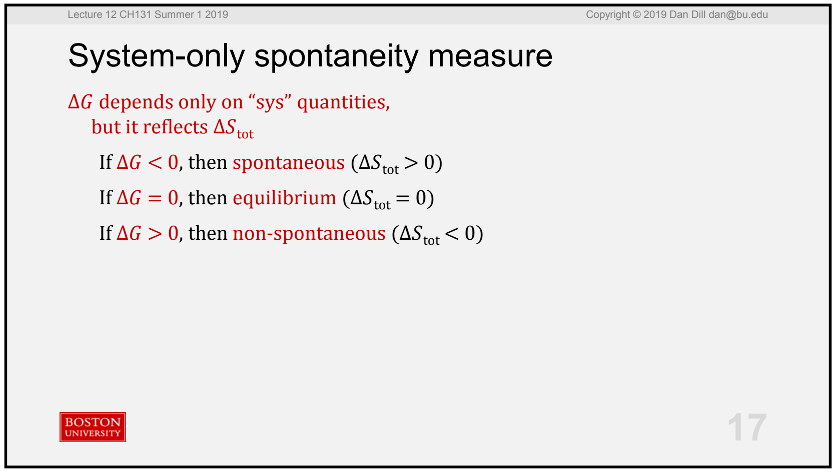
$$= +\Delta H_{sys} - T\Delta S_{sys}$$

Usually written with "sys" omitted

$\Delta G = \textcircled{\Delta H} - T\textcircled{\Delta S}$ from App D
" " "

with the understanding that

ΔH is ΔH_{sys} and ΔS is ΔS_{sys}



System-only spontaneity measure

ΔG depends only on "sys" quantities,
but it reflects ΔS_{tot}

If $\Delta G < 0$, then spontaneous ($\Delta S_{tot} > 0$)

If $\Delta G = 0$, then equilibrium ($\Delta S_{tot} = 0$)

If $\Delta G > 0$, then non-spontaneous ($\Delta S_{tot} < 0$)

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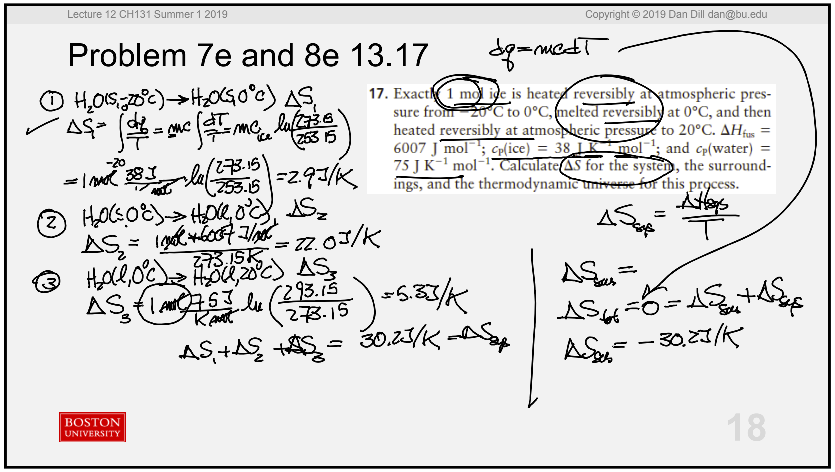

Problem 7e and 8e 13.17

$dq = mc\,dT$

17. Exactly 1 mol ice is heated reversibly at atmospheric pressure from −20°C to 0°C, melted reversibly at 0°C, and then heated reversibly at atmospheric pressure to 20°C. ΔH_{fus} = 6007 J mol^{-1}; c_P(ice) = 38 J K^{-1} mol^{-1}; and c_P(water) = 75 J K^{-1} mol^{-1}. Calculate ΔS for the system, the surroundings, and the thermodynamic universe for this process.

① $H_2O(s, -20°C) \rightarrow H_2O(s, 0°C)$ ΔS_1

✓ $\Delta S_1 = \int \frac{dq}{T} = mc\int \frac{dT}{T} = mc_{ice}\ln\left(\frac{273.15}{253.15}\right)$

$= 1\,\overset{-20}{\cancel{mol}}\,\frac{38\,J}{K\,\cancel{mol}}\ln\left(\frac{273.15}{253.15}\right) = 2.9\,J/K$

② $H_2O(s, 0°C) \rightarrow H_2O(l, 0°C)$ ΔS_2

$\Delta S_2 = \frac{1\,\cancel{mol} \times 6007\,J/\cancel{mol}}{273.15\,K} = 22.0\,J/K$

③ $H_2O(l, 0°C) \rightarrow H_2O(l, 20°C)$ ΔS_3

$\Delta S_3 = 1\,\cancel{mol}\,\frac{75\,J}{K\,\cancel{mol}}\ln\left(\frac{293.15}{273.15}\right) = 5.3\,J/K$

$\Delta S_1 + \Delta S_2 + \Delta S_3 = 30.2\,J/K = \Delta S_{sys}$

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

$\Delta S_{surr} =$

$\Delta S_{tot} = 0 = \Delta S_{surr} + \Delta S_{sys}$

$\Delta S_{surr} = -30.2\,J/K$

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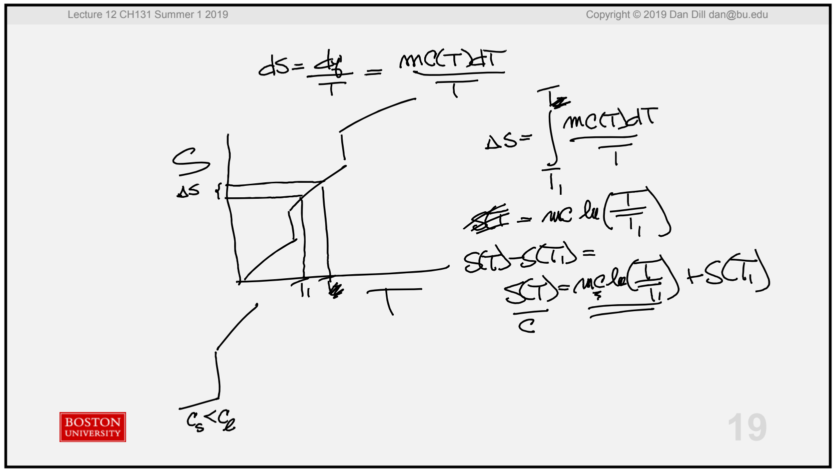

$dS = \frac{dq}{T} = \frac{mC(T)dT}{T}$

$\Delta S = \int_{T_1}^{T_2} \frac{mC(T)dT}{T}$

$\cancel{\Delta S} = mc\ln\left(\frac{T}{T_1}\right)$

$S(T) - S(T_1) =$

$S(T) = mc_s\ln\left(\frac{T}{T_1}\right) + S(T_1)$

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