

Module 8: Thermodynamics II, Lecture 3

Standard Molar Entropy



Learning Objective	Openstax 2e Chapter
Standard Molar Entropy (S^0)	<u>16.3</u>

Suggested Practice Problems

[Chapter 16 Exercises](#) – Questions: 21, 23, 25, 29 (use [Appendix G](#) for all questions)

Answers can be found in the [Chapter 16 Answer Key](#)

Absolute Entropy

Third Law of Thermodynamics

The entropy of a pure perfect crystal at 0 K is zero.

This makes sense in the context of Boltzmann's interpretation of entropy:

$$S = k_B \ln W$$

and in a perfect crystal at 0 K (no motion & perfect order),
there is only one ('frozen') microstate

- **Standard molar entropy** (at T) is the absolute entropy of one mole of a substance in its standard state at T temperature, denoted as $S^\circ(T)$.
- These S° values are then used to calculate $\Delta_r S^\circ(T)$, using the same Hess's Law learned in the Fall for H.

Standard molar entropy (S°) is non-zero for all substances.

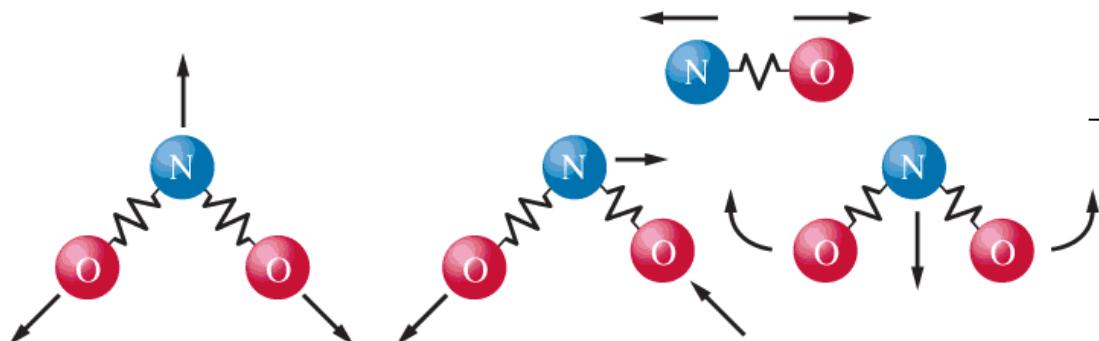
$$\frac{S^\circ(T)}{T}$$

0 K

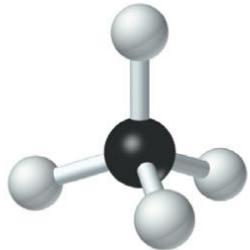
$$S^\circ = 0 \text{ J mol}^{-1} \text{ K}^{-1}$$

Standard Molar Entropy (S°)

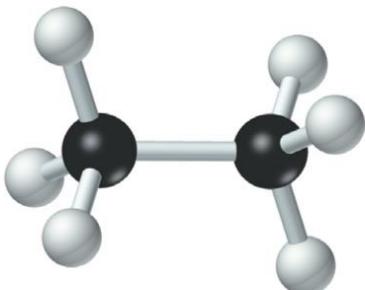
S° increases as molecular complexity increases (i.e., as the number of atoms per molecule increases).



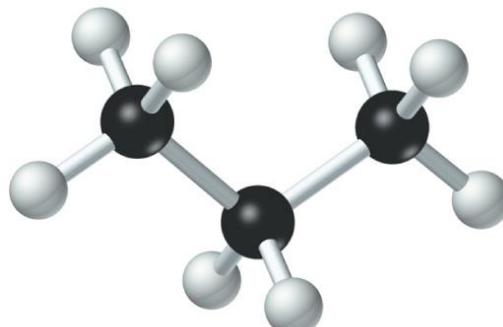
	S° , J mol ⁻¹ K ⁻¹
NO(g)	210.8
NO ₂ (g)	240.1



Methane, CH₄
 $S^\circ = 186.3 \text{ J mol}^{-1} \text{ K}^{-1}$

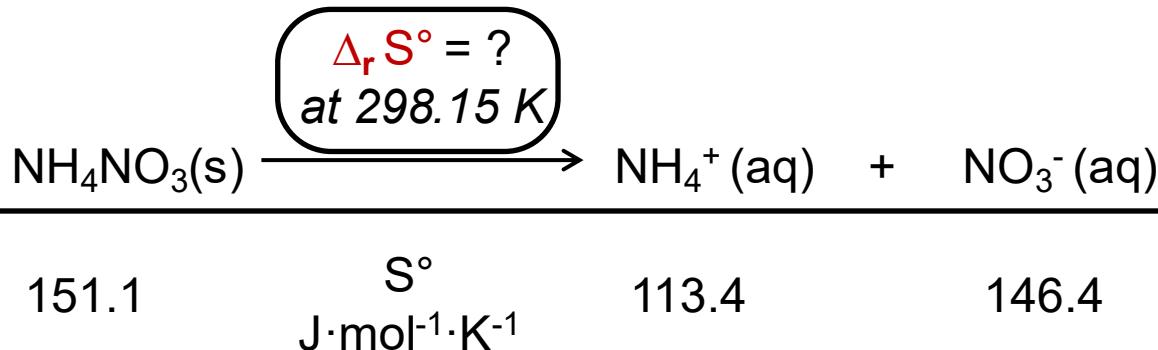


Ethane, C₂H₆
 $S^\circ = 229.6 \text{ J mol}^{-1} \text{ K}^{-1}$



Propane, C₃H₈
 $S^\circ = 270.3 \text{ J mol}^{-1} \text{ K}^{-1}$

Entropy Change in a Reaction ($\Delta_r S^\circ$)



Recall, Hess' Law: $\Delta_r H^\circ = \sum_i a_{i,products} \cdot \Delta H_{f,products}^\circ - \sum_j a_{j,reactants} \cdot \Delta H_{f,reactants}^\circ$

Similarly: $\Delta_r S^\circ = \sum_i a_{i,products} \cdot S_{products}^\circ - \sum_j a_{j,reactants} \cdot S_{reactants}^\circ$

$$\begin{aligned} \text{Therefore: } \Delta_r S^\circ &= S_{\text{NH}_4^+(\text{aq})}^\circ + S_{\text{NO}_3^-(\text{aq})}^\circ - S_{\text{NH}_4\text{NO}_3(\text{s})}^\circ \\ &= 113.4 \frac{\text{J}}{\text{mol}\cdot\text{K}} + 146.4 \frac{\text{J}}{\text{mol}\cdot\text{K}} - 151.1 \frac{\text{J}}{\text{mol}\cdot\text{K}} \\ &= 108.7 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \end{aligned}$$

Entropy Change in a Reaction ($\Delta_r S^\circ$)

What is the standard entropy change for the following reaction?

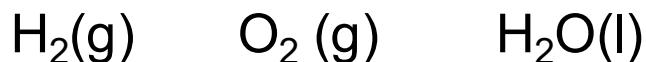


$$\begin{aligned}\Delta_r S^\circ &= 2 S^\circ_{\text{NO}_2\text{(g)}} - 2 S^\circ_{\text{NO(g)}} - S^\circ_{\text{O}_2\text{(g)}} \\&= 2 \left(240.1 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) - 2 \left(210.8 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) - \left(205.1 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \\&= -146.5 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

$\Delta S < 0$ Does it violate 2nd law of thermodynamics?

Criterion for a Spontaneous Change

Another spontaneous process.



$$\begin{aligned}\Delta_r S^\circ &= S^\circ_{\text{H}_2\text{O}(\text{l})} - S^\circ_{\text{H}_2(\text{g})} - \frac{1}{2} S^\circ_{\text{O}_2(\text{g})} \\ &= \left(69.91 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right) - \left(130.7 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right) - \frac{1}{2} \left(205.1 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right) \\ &= -163.3 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

$\Delta S < 0$ Does it violate 2nd law of thermodynamics?

ΔS_{system} alone is not a good indicator for spontaneous change!

Criterion for a Spontaneous Change

$$\Delta S_{total} = \Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

All spontaneous processes produce an increase in the entropy of the universe.

$$\Delta S_{univ} > 0$$

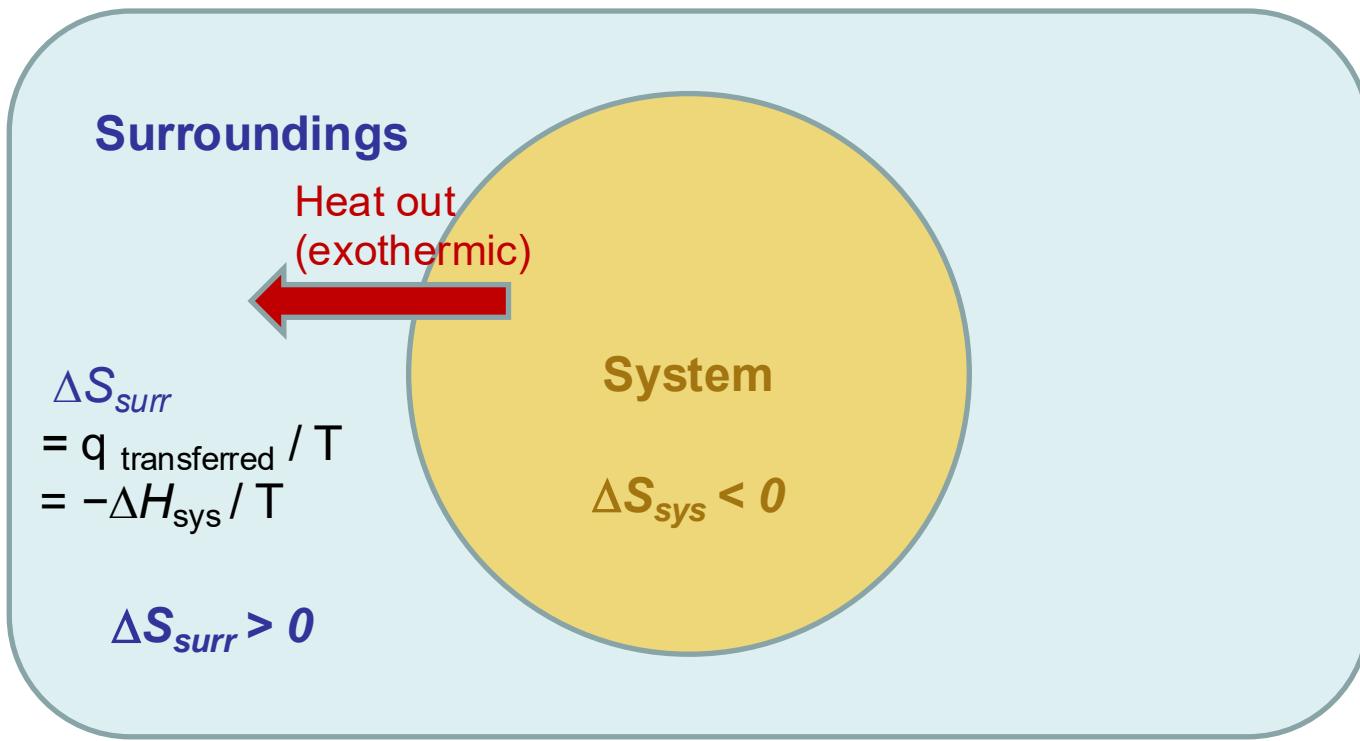
If $\Delta S_{univ} > 0$, the process is spontaneous.

If $\Delta S_{univ} < 0$, the process is not spontaneous.

If $\Delta S_{univ} = 0$, the process is reversible.

Criterion for a Spontaneous Change

$$\Delta S_{total} = \Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$



Note:

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

Only if T and P are constant
for the surroundings

$$\Delta S_{univ} > 0$$

Criterion for a Spontaneous Change

Recalling the spontaneous process to produce water from hydrogen gas and oxygen gas (Slide 6):



(This is ΔS_{sys})



Calculate ΔS_{univ} for this process under standard (SATP) conditions

$$\Delta S_{\text{surr}} = -\Delta H_{\text{sys}} / T = -(-285.8 \times 10^3 \text{ J mol}^{-1}) / 298.15 \text{ K} = 985.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = -163.3 \frac{\text{J}}{\text{mol}\cdot\text{K}} + 985.6 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

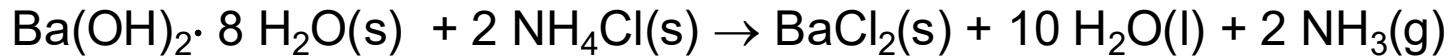
$$\Delta S_{\text{univ}} = 795.2 \text{ J mol}^{-1} \text{ K}^{-1}$$

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

This is why the process is spontaneous.

Additional Exercise

Calculate ΔS_{sys} and ΔS_{univ} for the following reaction under standard (SATP) conditions.

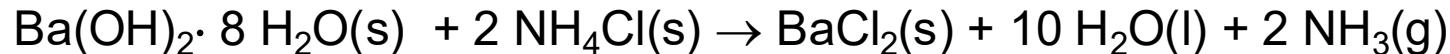


$$\Delta_r H^\circ = + 165 \text{ kJ mol}^{-1}$$

compound	$\text{Ba(OH)}_2 \cdot 8 \text{ H}_2\text{O(s)}$	$\text{NH}_4\text{Cl(s)}$	$\text{BaCl}_2\text{(s)}$	$\text{H}_2\text{O(l)}$	$\text{NH}_3\text{(g)}$
S° ($\text{J mol}^{-1} \text{ K}^{-1}$)	427	94.6	123.7	69.91	192.5

Additional Exercise

Calculate ΔS_{sys} and ΔS_{univ} for the following reaction under standard (SATP) conditions.



$$\Delta_r H^\circ = + 165 \text{ kJ mol}^{-1}$$

compound	$\text{Ba(OH)}_2 \cdot 8 \text{ H}_2\text{O(s)}$	$\text{NH}_4\text{Cl(s)}$	$\text{BaCl}_2\text{(s)}$	$\text{H}_2\text{O(l)}$	$\text{NH}_3\text{(g)}$
S° ($\text{J mol}^{-1} \text{ K}^{-1}$)	427	94.6	123.7	69.91	192.5

$$\Delta S_{sys}^0 = S_{\text{BaCl}_2}^0 + 10S_{\text{H}_2\text{O}}^0 + 2S_{\text{NH}_3}^0 - S_{\text{Ba(OH)}_2 \cdot 8 \text{ H}_2\text{O}}^0 - 2S_{\text{NH}_4\text{Cl}}^0$$

$$\Delta S_{sys}^0 = [123.7 + 10 \times 69.91 + 2 \times 192.5 - 427 - 2 \times 94.6] \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$\Delta S_{sys}^0 = 591.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta S_{sur}^0 = -\frac{\Delta_r H^0}{T}$$

$$\Delta S_{sur}^0 = -\frac{165 \text{ kJ} \cdot \text{mol}^{-1}}{298.15 \text{ K}}$$

$$\Delta S_{sur}^0 = -0.5534 \frac{\text{kJ}}{\text{mol} \cdot \text{K}} = -553.4 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta S_{univ}^0 = \Delta S_{sys}^0 + \Delta S_{sur}^0$$

$$\Delta S_{univ}^0 = 591.6 \frac{\text{J}}{\text{mol} \cdot \text{K}} - 553.5 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$\Delta S_{univ}^0 = 38.2 \text{ J mol}^{-1} \text{ K}^{-1}$$