

# ***Module 8: Thermodynamics II,***

## ***Lecture 3***

### **Standard Molar Entropy**



| Learning Objective               | Openstax 2e Chapter         |
|----------------------------------|-----------------------------|
| Standard Molar Entropy ( $S^0$ ) | <a href="#"><u>16.3</u></a> |

### **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

2

## 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

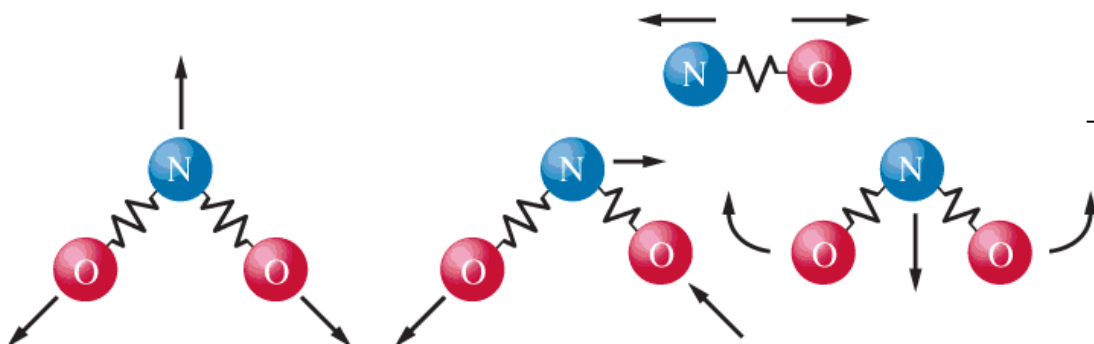
- **Standard molar entropy** (at T) is the absolute entropy of one mole of a substance in its standard state at T temperature, denoted as  $S^\circ(T)$ .
- These  $S^\circ$  values are then used to calculate  $\Delta_r S^\circ(T)$ , using the same Hess's Law learned in the Fall for H.

Standard molar entropy ( $S^\circ$ ) is non-zero for all substances.

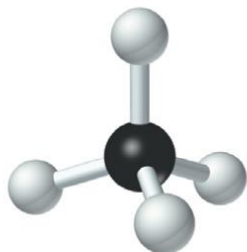
$$\begin{array}{c} S^\circ(T) \text{ --- } T \\ \uparrow \\ \text{--- } 0 K \\ S^\circ = 0 \text{ J mol}^{-1} \text{ K}^{-1} \end{array}$$

# Standard Molar Entropy ( $S^\circ$ )

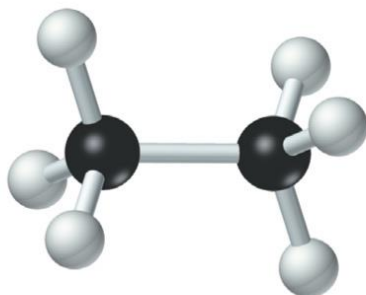
$S^\circ$  increases as molecular complexity increases (i.e., as the number of atoms per molecule increases).



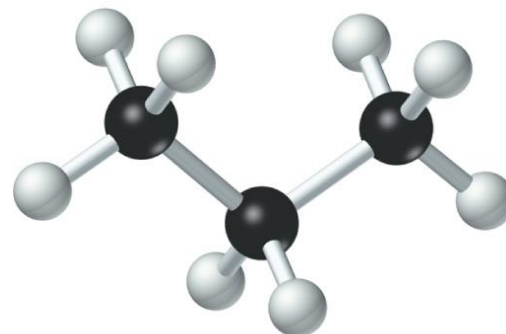
|                     | $S^\circ$ , J mol <sup>-1</sup> K <sup>-1</sup> |
|---------------------|---|
| NO(g)               | 210.8   |
| NO <sub>2</sub> (g) | 240.1   |



Methane, CH<sub>4</sub>  
 $S^\circ = 186.3 \text{ J mol}^{-1} \text{ K}^{-1}$

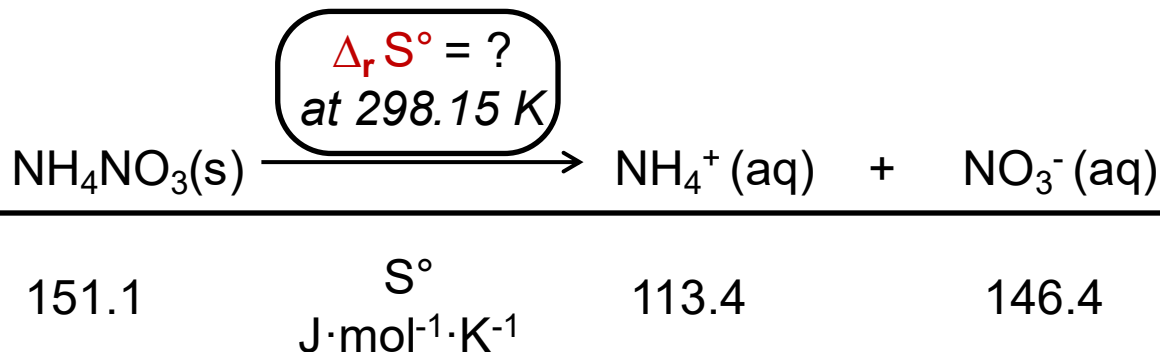


Ethane, C<sub>2</sub>H<sub>6</sub>  
 $S^\circ = 229.6 \text{ J mol}^{-1} \text{ K}^{-1}$



Propane, C<sub>3</sub>H<sub>8</sub>  
 $S^\circ = 270.3 \text{ J mol}^{-1} \text{ K}^{-1}$

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



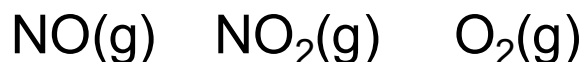
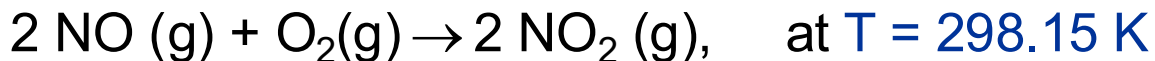
Recall, Hess' Law: 
$$\Delta_r H^\circ = \sum_i a_{i,\text{products}} \cdot \Delta H_{f,\text{products}}^\circ - \sum_j a_{j,\text{reactants}} \cdot \Delta H_{f,\text{reactants}}^\circ$$

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

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

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

What is the standard entropy change for the following reaction?



|   |       |       |       |
|---|-------|-------|-------|
| $S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> ): | 210.8 | 240.1 | 205.1 |
|---|-------|-------|-------|

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

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

# Criterion for a Spontaneous Change

Another spontaneous process.



|   | $\text{H}_2(\text{g})$ | $\text{O}_2(\text{g})$ | $\text{H}_2\text{O}(\text{l})$ |
|---|------------------------|------------------------|--------------------------------|
| $S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> ): | 130.7                  | 205.1                  | 69.91                          |

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

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

$\Delta S_{\text{system}}$  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.

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

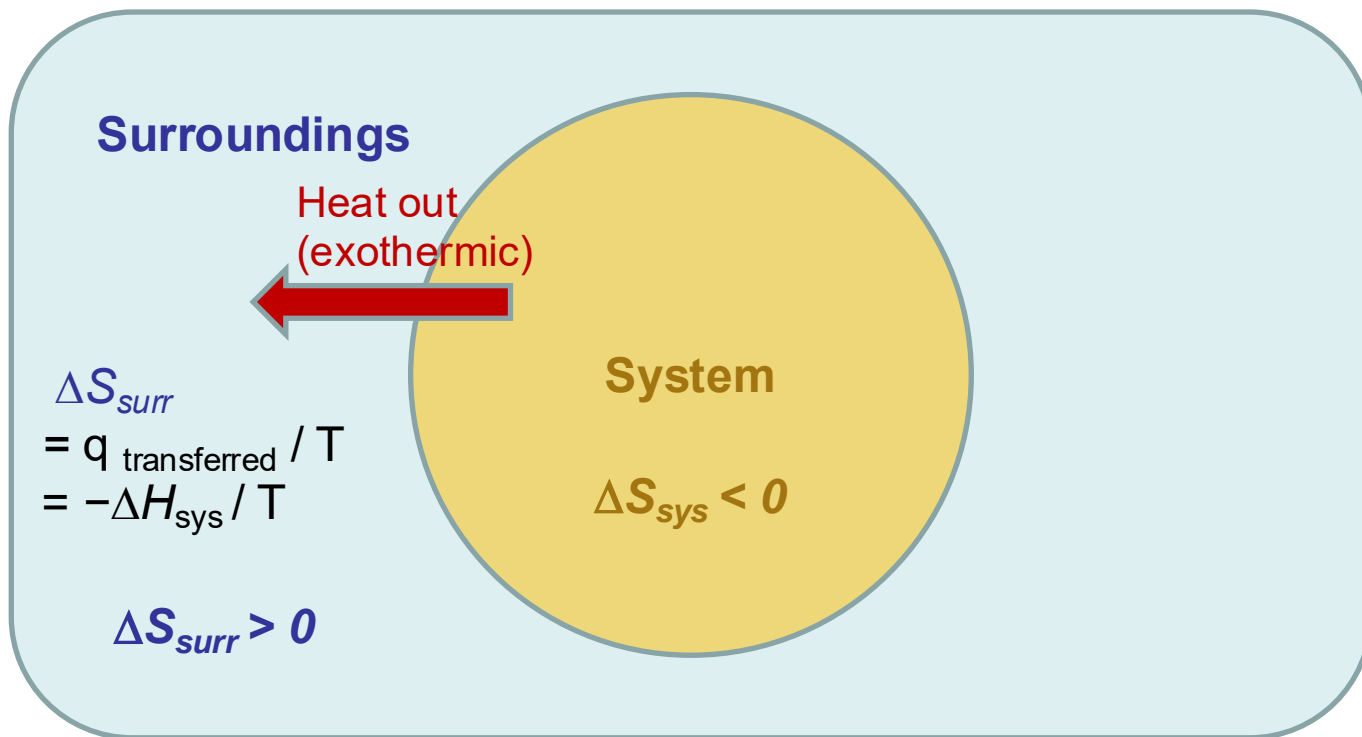
If  $\Delta S_{univ} > 0$ , the process is spontaneous.

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:

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

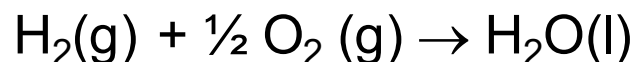
Only if T and P are constant  
for the surroundings

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



# Criterion for a Spontaneous Change

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



$$\Delta_r S^\circ = -163.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

(This is  $\Delta S_{\text{sys}}$ )

$$\Delta_r H^\circ = -285.8 \text{ kJ mol}^{-1}$$

$\Delta H_{\text{sys}}$  (Thermochemistry learned in the Fall)

**Calculate  $\Delta S_{\text{univ}}$**  for this process under standard (SATP) conditions

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

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

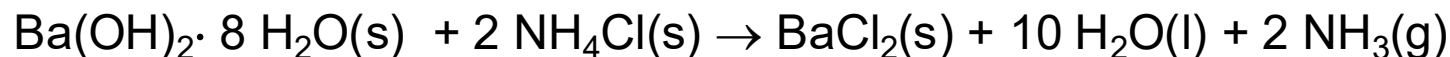
$$\Delta S_{\text{univ}} = 795.2 \text{ J mol}^{-1} \text{ K}^{-1}$$

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

This is why the process is spontaneous.

## Additional Exercise

Calculate  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{univ}}$  for the following reaction under standard (SATP) conditions.

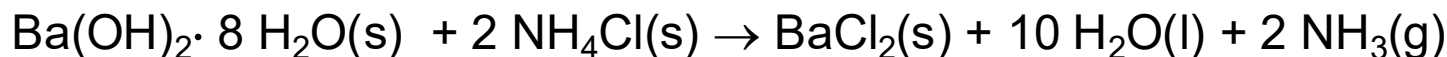


$$\Delta_r H^\circ = + 165 \text{ kJ mol}^{-1}$$

| compound  | Ba(OH) <sub>2</sub> · 8 H <sub>2</sub> O(s) | NH <sub>4</sub> Cl(s) | BaCl <sub>2</sub> (s) | H <sub>2</sub> O(l) | NH <sub>3</sub> (g) |
|---|---|-----------------------|-----------------------|---------------------|---------------------|
| <b>S°</b><br>(J mol <sup>-1</sup> K <sup>-1</sup> ) | 427   | 94.6                  | 123.7                 | 69.91               | 192.5               |

## Additional Exercise

Calculate  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{univ}}$  for the following reaction under standard (SATP) conditions.



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

| compound  | $\text{Ba(OH)}_2 \cdot 8 \text{H}_2\text{O(s)}$ | $\text{NH}_4\text{Cl(s)}$ | $\text{BaCl}_2\text{(s)}$ | $\text{H}_2\text{O(l)}$ | $\text{NH}_3\text{(g)}$ |
|---|---|---------------------------|---------------------------|-------------------------|-------------------------|
| <b><math>S^\circ</math></b><br>(J mol <sup>-1</sup> K <sup>-1</sup> ) | 427   | 94.6                      | 123.7                     | 69.91                   | 192.5                   |

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

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

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

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

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

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

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

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

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