

## 19.4: Predicting Entropy and Entropy Changes for Chemical Reactions

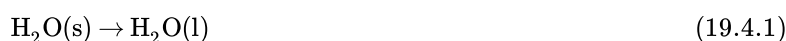
### Learning Objectives

- To calculate entropy changes for a chemical reaction

We have seen that the energy given off (or absorbed) by a reaction, and monitored by noting the change in temperature of the surroundings, can be used to determine the enthalpy of a reaction (e.g. by using a calorimeter). Tragically, there is no comparable easy way to experimentally measure the change in entropy for a reaction. Suppose we know that energy is going into a system (or coming out of it), and yet we do not observe any change in temperature. What is going on in such a situation? Changes in internal energy, that are not accompanied by a temperature change, might reflect changes in the entropy of the system.

For example, consider water at  $^{\circ}\text{C}$  at 1 atm pressure

- This is the temperature and pressure condition where liquid and solid phases of water are in equilibrium (also known as the melting point of ice)



- At such a temperature and pressure we have a situation (by definition) where we have some ice and some liquid water
- If a small amount of energy is input into the system the equilibrium will shift slightly to the right (i.e. in favor of the liquid state)
- Likewise if a small amount of energy is withdrawn from the system, the equilibrium will shift to the left (more ice)

*However, in both of the above situations, the energy change is not accompanied by a change in temperature (the temperature will not change until we no longer have an equilibrium condition; i.e. all the ice has melted or all the liquid has frozen)*

Since the quantitative term that relates the amount of heat energy input vs. the rise in temperature is the heat capacity, it would seem that in some way, information about the heat capacity (and how it changes with temperature) would allow us to determine the entropy change in a system. In fact, values for the "standard molar entropy" of a substance have units of J/mol K, the same units as for molar heat capacity.

### Standard Molar Entropy, $S^{\circ}$

The entropy of a substance has an absolute value of 0 entropy at 0 K.

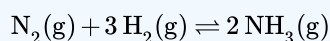
- Standard molar entropies** are listed for a reference temperature (like 298 K) and 1 atm pressure (i.e. the entropy of a pure substance at 298 K and 1 atm pressure). A table of standard molar entropies at 0K would be pretty useless because it would be 0 for every substance (duh!) Standard molar entropy values are listed for a variety of substances in [Table T2](#).
- When comparing standard molar entropies for a substance that is either a solid, liquid or gas at 298 K and 1 atm pressure, the gas will have more entropy than the liquid, and the liquid will have more entropy than the solid
- Unlike *enthalpies of formation*, standard molar entropies of elements are not 0.

The entropy change in a chemical reaction is given by the sum of the entropies of the products minus the sum of the entropies of the reactants. As with other calculations related to balanced equations, the coefficients of each component must be taken into account in the entropy calculation (the  $n$ , and  $m$ , terms below are there to indicate that the coefficients must be accounted for):

$$\Delta S^{\circ} = \sum_n nS^{\circ}(\text{products}) - \sum_m mS^{\circ}(\text{reactants})$$

### ✓ Example 19.4.1: Haber Process

Calculate the change in entropy associated with the Haber process for the production of ammonia from nitrogen and hydrogen gas.



At 298K as a standard temperature:

- $S^0(\text{NH}_3) = 192.5 \text{ J/mol K}$
- $S^0(\text{H}_2) = 130.6 \text{ J/mol K}$
- $S^0(\text{N}_2) = 191.5 \text{ J/mol K}$

### Solution

From the balanced equation we can write the equation for  $\Delta S^0$  (the change in the standard molar entropy for the reaction):

$$\Delta S^0 = 2 \cdot S^0(\text{NH}_3) - [S^0(\text{N}_2) + (3 \cdot S^0(\text{H}_2))]$$

$$\Delta S^0 = 2 \cdot 192.5 - [191.5 + (3 \cdot 130.6)]$$

$$\Delta S^0 = -198.3 \text{ J/mol K}$$

It would appear that the process results in a **decrease** in entropy - i.e. a decrease in disorder. This is expected because we are decreasing the number of gas molecules. In other words the  $\text{N}_2(\text{g})$  used to float around independently of the  $\text{H}_2$  gas molecules. After the reaction, the two are bonded together and can't float around freely from one another. (I guess you can consider marriage as a negative entropy process!)

To calculate  $\Delta S^0$  for a chemical reaction from standard molar entropies, we use the familiar “products minus reactants” rule, in which the absolute entropy of each reactant and product is multiplied by its stoichiometric coefficient in the balanced chemical equation. Example 19.4.2 illustrates this procedure for the combustion of the liquid hydrocarbon isooctane ( $\text{C}_8\text{H}_{18}$ ; 2,2,4-trimethylpentane).

$\Delta S^0$  for a reaction can be calculated from absolute entropy values using the same “products minus reactants” rule used to calculate  $\Delta H^0$ .

### ✓ Example 19.4.2: Combustion of Octane

Use the data in [Table T2](#) to calculate  $\Delta S^0$  for the combustion reaction of liquid isooctane with  $\text{O}_2(\text{g})$  to give  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  at 298 K.

**Given:** standard molar entropies, reactants, and products

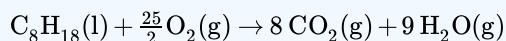
**Asked for:**  $\Delta S^0$

**Strategy:**

Write the balanced chemical equation for the reaction and identify the appropriate quantities in [Table T2](#). Subtract the sum of the absolute entropies of the reactants from the sum of the absolute entropies of the products, each multiplied by their appropriate stoichiometric coefficients, to obtain  $\Delta S^0$  for the reaction.

**Solution:**

The balanced chemical equation for the complete combustion of isooctane ( $\text{C}_8\text{H}_{18}$ ) is as follows:



We calculate  $\Delta S^0$  for the reaction using the “products minus reactants” rule, where m and n are the stoichiometric coefficients of each product and each reactant:

$$\begin{aligned} \Delta S_{\text{rxn}}^0 &= \sum m S^0(\text{products}) - \sum n S^0(\text{reactants}) \\ &= [8 S^0(\text{CO}_2) + 9 S^0(\text{H}_2\text{O})] - [S^0(\text{C}_8\text{H}_{18}) + \frac{25}{2} S^0(\text{O}_2)] \\ &= \{ [8 \text{ mol CO}_2 \times 213.8 \text{ J}/(\text{mol} \cdot \text{K})] + [9 \text{ mol H}_2\text{O} \times 188.8 \text{ J}/(\text{mol} \cdot \text{K})] \} \\ &\quad - \left\{ [1 \text{ mol C}_8\text{H}_{18} \times 329.3 \text{ J}/(\text{mol} \cdot \text{K})] + \left[ \frac{25}{2} \text{ mol O}_2 \times 205.2 \text{ J}/(\text{mol} \cdot \text{K}) \right] \right\} \\ &= 515.3 \text{ J/K} \end{aligned}$$

$\Delta S^0$  is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

### ? Exercise 19.4.2

Use the data in [Table T2](#) to calculate  $\Delta S^\circ$  for the reaction of  $\text{H}_2(\text{g})$  with liquid benzene ( $\text{C}_6\text{H}_6$ ) to give cyclohexane ( $\text{C}_6\text{H}_{12}$ ).

**Answer**

-361.1 J/K



Calculating the Entropy of Reaction using S: [Calculating the Entropy of Reaction using S\(opens in new window\)](#) [youtu.be]

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