

## 16.3: The Second and Third Laws of Thermodynamics

### Learning Objectives

- State and explain the second and third laws of thermodynamics
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

### 16.3.1: The Second Law of Thermodynamics

In the quest to identify a property that may reliably predict the spontaneity of a process, we have identified a very promising candidate: entropy. Processes that involve an increase in entropy of *the system* ( $\Delta S > 0$ ) are very often spontaneous; however, examples to the contrary are plentiful. By expanding consideration of entropy changes to include *the surroundings*, we may reach a significant conclusion regarding the relation between this property and spontaneity. In thermodynamic models, the system and surroundings comprise everything, that is, the universe, and so the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \quad (16.3.1)$$

To illustrate this relation, consider again the process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. *This is always observed to occur spontaneously.* Designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}} \quad (16.3.2)$$

The arithmetic signs of  $q_{\text{rev}}$  denote the loss of heat by the system and the gain of heat by the surroundings. Since  $T_{\text{sys}} > T_{\text{surr}}$  in this scenario, the magnitude of the entropy change for the surroundings will be greater than that for the system, and so the sum of  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$  will yield a positive value for  $\Delta S_{\text{univ}}$ . *This process involves an increase in the entropy of the universe.*

2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. *This is never observed to occur spontaneously.* Again designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}} \quad (16.3.3)$$

The arithmetic signs of  $q_{\text{rev}}$  denote the gain of heat by the system and the loss of heat by the surroundings. The magnitude of the entropy change for the surroundings will again be greater than that for the system, but in this case, the signs of the heat changes will yield a negative value for  $\Delta S_{\text{univ}}$ . *This process involves a decrease in the entropy of the universe.*

3. The temperature difference between the objects is infinitesimally small,  $T_{\text{sys}} \approx T_{\text{surr}}$ , and so the heat flow is thermodynamically reversible. See the previous section's discussion). In this case, the system and surroundings experience entropy changes that are equal in magnitude and therefore sum to yield a value of zero for  $\Delta S_{\text{univ}}$ . *This process involves no change in the entropy of the universe.*

These results lead to a profound statement regarding the relation between entropy and spontaneity known as the second law of thermodynamics: *all spontaneous changes cause an increase in the entropy of the universe.* A summary of these three relations is provided in Table 16.3.1.

Table 16.3.1: The Second Law of Thermodynamics

$\Delta S_{\text{univ}} > 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{\text{univ}} = 0$	reversible (system is at equilibrium)

*All spontaneous changes cause an increase in the entropy of the universe.*

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For

example, combustion of a fuel in air involves transfer of heat from a system (the fuel and oxygen molecules undergoing reaction) to surroundings that are infinitely more massive (the earth's atmosphere). As a result,  $q_{surr}$  is a good approximation of  $q_{rev}$ , and the second law may be stated as the following:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + \frac{q_{surr}}{T} \quad (16.3.4)$$

We may use this equation to predict the spontaneity of a process as illustrated in Example 16.3.1.

### ✓ Example 16.3.1: Will Ice Spontaneously Melt?

The entropy change for the process



is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at  $-10.00^\circ\text{C}$ ? Is it spontaneous at  $+10.00^\circ\text{C}$ ?

#### Solution

We can assess the spontaneity of the process by calculating the entropy change of the universe. If  $\Delta S_{univ}$  is positive, then the process is spontaneous. At both temperatures,  $\Delta S_{sys} = 22.1 \text{ J/K}$  and  $q_{surr} = -6.00 \text{ kJ}$ .

At  $-10.00^\circ\text{C}$  (263.15 K), the following is true:

$$\begin{aligned} \Delta S_{univ} &= \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + \frac{q_{surr}}{T} \\ &= 22.1 \text{ J/K} + \frac{-6.00 \times 10^3 \text{ J}}{263.15 \text{ K}} = -0.7 \text{ J/K} \end{aligned}$$

$S_{univ} < 0$ , so melting is nonspontaneous (*not* spontaneous) at  $-10.0^\circ\text{C}$ .

At  $10.00^\circ\text{C}$  (283.15 K), the following is true:

$$\begin{aligned} \Delta S_{univ} &= \Delta S_{sys} + \frac{q_{surr}}{T} \\ &= 22.1 \text{ J/K} + \frac{-6.00 \times 10^3 \text{ J}}{283.15 \text{ K}} = +0.9 \text{ J/K} \end{aligned}$$

$S_{univ} > 0$ , so melting is spontaneous at  $10.00^\circ\text{C}$ .

### ? Exercise 16.3.1

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of  $S_{univ}$ ?

#### Answer

Entropy is a state function, and freezing is the opposite of melting. At  $-10.00^\circ\text{C}$  spontaneous,  $+0.7 \text{ J/K}$ ; at  $+10.00^\circ\text{C}$  nonspontaneous,  $-0.9 \text{ J/K}$ .

## 16.3.2: The Third Law of Thermodynamics

The previous section described the various contributions of matter and energy dispersal that contribute to the entropy of a system. With these contributions in mind, consider the entropy of a pure, perfectly crystalline solid possessing no kinetic energy (that is, at a temperature of absolute zero, 0 K). This system may be described by a single microstate, as its purity, perfect crystallinity and complete lack of motion means there is but one possible location for each identical atom or molecule comprising the crystal ( $W = 1$ ). According to the Boltzmann equation, the entropy of this system is zero.

$$S = k \ln W = k \ln(1) = 0 \quad (16.3.5)$$

This limiting condition for a system's entropy represents the third law of thermodynamics: *the entropy of a pure, perfect crystalline substance at 0 K is zero.*

### Definition: Third Law of Thermodynamics

*The entropy of a pure, perfect crystalline substance at 0 K is zero.*

We can make careful calorimetric measurements to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. Standard entropies are given the label  $S_{298}^{\circ}$  for values determined for one mole of substance, isolated in its pure form in its own container, at a pressure of 1 bar and a temperature of 298 K.

### Definition: Term

The thermodynamic standard state of a substance refers to an isolated sample of that substance, in its own container, at 1.000 bar (0.9869 atm) pressure. If the substance is a solute, the most common standard state is one in which the concentration of the solute is 1.000 molal (sometimes approximated with 1.000 M). There is no defined temperature for the standard state, but most discussions about standard state assume that the temperature is 298.15 K (25°C) unless otherwise noted.

This may seem like a strange definition, because it requires that each of the reactants and each of the products of a reaction are kept separate from one another, unmixed. The entropy of mixing must be determined separately.

The standard entropy change ( $\Delta S^{\circ}$ ) for any process may be computed from the standard entropies of its reactant and product species like the following:

$$\Delta S^{\circ} = \sum \nu S_{298}^{\circ}(\text{products}) - \sum \nu S_{298}^{\circ}(\text{reactants}) \quad (16.3.6)$$

Here,  $\nu$  represents stoichiometric coefficients in the balanced equation representing the process. For example,  $\Delta S^{\circ}$  for the following reaction at room temperature



is computed as the following:

$$= [xS_{298}^{\circ}(C) + yS_{298}^{\circ}(D)] - [mS_{298}^{\circ}(A) + nS_{298}^{\circ}(B)] \quad (16.3.8)$$

Table 16.3.2 lists some standard entropies at 298.15 K. You can find additional standard entropies in Tables T1 or T2.

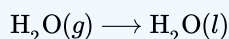
Table 16.3.2: Standard Entropies (at 298.15 K, 1 atm)

Substance	$S_{298}^{\circ} \frac{J}{mol K}$
<i>carbon</i>	
C(s, graphite)	5.740
C(s, diamond)	2.38
CO(g)	197.7
CO <sub>2</sub> (g)	213.8
CH <sub>4</sub> (g)	186.3
C <sub>2</sub> H <sub>4</sub> (g)	219.5
C <sub>2</sub> H <sub>6</sub> (g)	229.5
CH <sub>3</sub> OH(l)	126.8
C <sub>2</sub> H <sub>5</sub> OH(l)	160.7
<i>hydrogen</i>	
H <sub>2</sub> (g)	130.57
H(g)	114.6

Substance	$S_{298}^{\circ} \frac{J}{mol \cdot K}$
$H_2O(g)$	188.71
$H_2O(l)$	69.91
$HCl(g)$	186.8
$H_2S(g)$	205.7
oxygen	
$O_2(g)$	205.03

### ✓ Example 16.3.2: Determination of $\Delta S^{\circ}$

Calculate the standard entropy change for the following process:



#### Solution

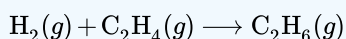
The value of the standard entropy change at room temperature,  $\Delta S_{298}^{\circ}$ , is the difference between the standard entropy of the product,  $H_2O(l)$ , and the standard entropy of the reactant,  $H_2O(g)$ .

$$\begin{aligned}\Delta S_{298}^{\circ} &= S_{298}^{\circ}(H_2O(l)) - S_{298}^{\circ}(H_2O(g)) \\ &= (70.0 \text{ J mol}^{-1} \text{ K}^{-1}) - (188.8 \text{ J mol}^{-1} \text{ K}^{-1}) = -118.8 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

The value for  $\Delta S_{298}^{\circ}$  is negative, as expected for this phase transition (condensation), which the previous section discussed.

### ? Exercise 16.3.2

Calculate the standard entropy change for the following process:

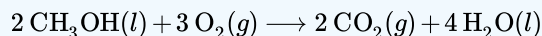


#### Answer

$$-120.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

### ✓ Example 16.3.3: Determination of $\Delta S^{\circ}$

Calculate the standard entropy change for the combustion of methanol,  $CH_3OH$  at room temperature:



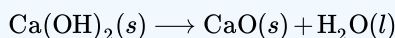
#### Solution

The value of the standard entropy change is equal to the difference between the standard entropies of the products and the entropies of the reactants scaled by their stoichiometric coefficients.

$$\begin{aligned}\Delta S^{\circ} &= \Delta S_{298}^{\circ} = \sum \nu S_{298}^{\circ}(\text{products}) - \sum \nu S_{298}^{\circ}(\text{reactants}) \\ &= [2S_{298}^{\circ}(CO_2(g)) + 4S_{298}^{\circ}(H_2O(l))] - [2S_{298}^{\circ}(CH_3OH(l)) + 3S_{298}^{\circ}(O_2(g))] \\ &= \{[2(213.8) + 4 \times 70.0] - [2(126.8) + 3(205.03)]\} = -161.1 \text{ J/mol} \cdot \text{K}\end{aligned}$$

### ? Exercise 16.3.3

Calculate the standard entropy change for the following reaction:



**Answer**

24.7 J/mol•K

## Summary

The second law of thermodynamics states that a spontaneous process increases the entropy of the universe,  $S_{\text{univ}} > 0$ . If  $\Delta S_{\text{univ}} < 0$ , the process is nonspontaneous, and if  $\Delta S_{\text{univ}} = 0$ , the system is at equilibrium. The third law of thermodynamics establishes the zero for entropy as that of a perfect, pure crystalline solid at 0 K. With only one possible microstate, the entropy is zero. We may compute the standard entropy change for a process by using standard entropy values for the reactants and products involved in the process.

### 16.3.3: Key Equations

- $\Delta S^\circ = \Delta S_{298}^\circ = \sum \nu S_{298}^\circ(\text{products}) - \sum \nu S_{298}^\circ(\text{reactants})$
- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$

## Glossary

**second law of thermodynamics**

entropy of the universe increases for a spontaneous process

**standard entropy ( $S^\circ$ )**

entropy for a substance at 1 bar pressure; tabulated values are usually determined at 298.15 K and denoted  $S_{298}^\circ$

**standard entropy change ( $\Delta S^\circ$ )**

change in entropy for a reaction calculated using the standard entropies, usually at room temperature and denoted  $\Delta S_{298}^\circ$

**third law of thermodynamics**

entropy of a perfect crystal at absolute zero (0 K) is zero

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