

2.2.5: The Second and Third Laws of Thermodynamics

Learning Objectives

By the end of this section, you will be able to:

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

The Second Law of Thermodynamics

In the quest to identify a property that may reliably predict the spontaneity of a process, a promising candidate has been identified: 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:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

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:

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

The magnitudes of $-q_{\text{rev}}$ and q_{rev} are equal, their opposite arithmetic signs denoting loss of heat by the system and gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the entropy *decrease* of the system will be less than the entropy *increase* of the surroundings, and so *the entropy of the universe will increase*:

$$|\Delta S_{\text{sys}}| < |\Delta S_{\text{surr}}|$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

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:

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

The arithmetic signs of q_{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 (that is, *the direction of the heat flow*) will yield a negative value for ΔS_{univ} . *This process involves a decrease in the entropy of the universe.*

3. The objects are at essentially the same temperature, $T_{\text{sys}} \approx T_{\text{surr}}$, and so the magnitudes of the entropy changes are essentially the same for both the system and the surroundings. In this case, the entropy change of the universe is zero, and the system is *at equilibrium*.

$$|\Delta S_{\text{sys}}| \approx |\Delta S_{\text{surr}}|$$

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

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 2.2.5.1.

Table 2.2.5.1: The Second Law of Thermodynamics

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

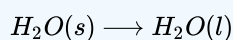
For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For example, combustion of a fuel in air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

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$$

We may use this equation to predict the spontaneity of a process as illustrated in Example 2.2.5.1.

✓ Example 2.2.5.1: 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°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 ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, $\Delta S_{\text{sys}} = 22.1 \text{ J/K}$ and $q_{\text{surr}} = -6.00 \text{ kJ}$.

At -10.00°C (263.15 K), the following is true:

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

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

At 10.00°C (283.15 K), the following is true:

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

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

? Exercise 2.2.5.1

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, so $\Delta S_{\text{freezing}} = -\Delta S_{\text{melting}} = -22.1 \text{ J/K}$ and $q_{\text{surr}} = +6.00 \text{ kJ}$. At -10.00°C spontaneous, $+0.7 \text{ J/K}$; at $+10.00^\circ\text{C}$ nonspontaneous, -0.9 J/K .

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.

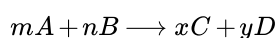
$$S = k \ln W = k \ln(1) = 0$$

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.*

Careful calorimetric measurements can be made to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. **Standard entropies** (S°) are for one mole of substance under standard conditions (a pressure of 1 bar and a temperature of 298.15 K; see details regarding standard conditions in the thermochemistry chapter of this text). The **standard entropy change** (ΔS°) for a reaction may be computed using standard entropies as shown below:

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

where ν represents stoichiometric coefficients in the balanced equation representing the process. For example, ΔS° for the following reaction at room temperature



is computed as:

$$= [xS^\circ(C) + yS^\circ(D)] - [mS^\circ(A) + nS^\circ(B)]$$

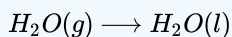
A partial listing of standard entropies is provided in Table 2.2.5.2 and additional values are provided in Appendix G. The example exercises that follow demonstrate the use of S° values in calculating standard entropy changes for physical and chemical processes.

Table 2.2.5.2: Standard entropies for selected substances measured at 1 atm and 298.15 K. (Values are approximately equal to those measured at 1 bar, the currently accepted standard state pressure.)

Substance	(J mol ⁻¹ K ⁻¹)
carbon	
C(s, graphite)	5.740
C(s, diamond)	2.38
CO(g)	197.7
CO ₂ (g)	213.8
CH ₄ (g)	186.3
C ₂ H ₄ (g)	219.5
C ₂ H ₆ (g)	229.5
CH ₃ OH(l)	126.8
C ₂ H ₅ OH(l)	160.7
hydrogen	
H ₂ (g)	130.57
H(g)	114.6
H ₂ O(g)	188.71
H ₂ O(l)	69.91
HCl(g)	186.8
H ₂ S(g)	205.7
oxygen	
O ₂ (g)	205.03

✓ Example 2.2.5.2: Determination of ΔS°

Calculate the standard entropy change for the following process:



Solution

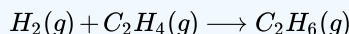
Calculate the entropy change using standard entropies as shown above:

$$\Delta S^\circ = (1\text{mol}) (70.0\text{Jmol}^{-1}\text{K}^{-1}) - (1\text{mol}) (188.8\text{Jmol}^{-1}\text{K}^{-1}) = -118.8\text{J/K}$$

The value for ΔS° is negative, as expected for this phase transition (condensation), which the previous section discussed.

? Exercise 2.2.5.2

Calculate the standard entropy change for the following process:

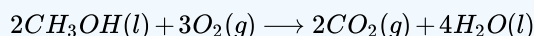


Answer

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

✓ Example 2.2.5.3: Determination of ΔS°

Calculate the standard entropy change for the combustion of methanol, CH_3OH :



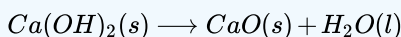
Solution

Calculate the entropy change using standard entropies as shown above:

$$\begin{aligned}\Delta S^\circ &= \sum \nu S^\circ(\text{products}) - \sum \nu S^\circ(\text{reactants}) \\ &= [2\text{mol} \times S^\circ(\text{CO}_2(g)) + 4\text{mol} \times S^\circ(\text{H}_2\text{O}(l))] - [2\text{mol} \times S^\circ(\text{CH}_3\text{OH}(l)) + 3\text{mol} \times S^\circ(\text{O}_2(g))] \\ &= \{[2(213.8) + 4 \times 70.0] - [2(126.8) + 3(205.2)]\} = -161.6\text{J/K}\end{aligned}$$

? Exercise 2.2.5.3

Calculate the standard entropy change for the following reaction:



Answer

$$24.7\text{ J/K}$$

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