

8.4: Criteria for Spontaneous Change- The Second Law 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

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:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \quad (8.4.1)$$

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:

$$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}} \quad (8.4.2)$$

The arithmetic signs of q_{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 ΔS_{sys} and ΔS_{surr} will yield a positive value for ΔS_{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:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}} \quad (8.4.3)$$

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 will yield a negative value for ΔS_{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 ΔS_{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 8.4.1.

Table 8.4.1: 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)

Definition: The Second Law of Thermodynamics

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:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \quad (8.4.4)$$

We may use this equation to predict the spontaneity of a process as illustrated in Example 8.4.1.

✓ 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 8.4.1

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°C spontaneous, $+0.7 \text{ J/K}$; at $+10.00^\circ\text{C}$ nonspontaneous, -0.9 J/K .

Gibbs Energy and Changes of Gibbs Energy

One of the challenges of using the second law of thermodynamics to determine if a process is spontaneous is that we must determine the entropy change for the system *and* the entropy change for the surroundings. An alternative approach involving a new thermodynamic property defined in terms of system properties only was introduced in the late nineteenth century by American mathematician Josiah Willard Gibbs. This new property is called the Gibbs free energy change (G) (or simply the *free energy*), and it is defined in terms of a system's enthalpy and entropy as the following:

$$G = H - TS \quad (8.4.5)$$

Free energy is a state function, and at constant temperature and pressure, the standard free energy change (ΔG°) may be expressed as the following:

$$\Delta G = \Delta H - T\Delta S \quad (8.4.6)$$

(For simplicity's sake, the subscript "sys" will be omitted henceforth.) We can understand the relationship between this system property and the spontaneity of a process by recalling the previously derived second law expression:

$$\Delta S_{\text{univ}} = \Delta S + \frac{q_{\text{surr}}}{T} \quad (8.4.7)$$

The first law requires that $q_{\text{surr}} = -q_{\text{sys}}$, and at constant pressure $q_{\text{sys}} = \Delta H$, and so this expression may be rewritten as the following:

$$\Delta S_{\text{univ}} = \Delta S - \frac{\Delta H}{T} \quad (8.4.8)$$

ΔH is the enthalpy change of the system. Multiplying both sides of this equation by $-T$, and rearranging yields the following:

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S \quad (8.4.9)$$

Comparing this equation to the previous one for free energy change shows the following relation:

$$\Delta G = -T\Delta S_{\text{univ}} \quad (8.4.10)$$

The free energy change is therefore a reliable indicator of the spontaneity of a process, being directly related to the previously identified spontaneity indicator, ΔS_{univ} . Table 8.4.2 expands on Table 8.4.2 and summarizes the relation between the spontaneity of a process and the arithmetic signs of ΔG and ΔS indicators.

Table 8.4.2: Relation between Process Spontaneity and Signs of Thermodynamic Properties

$\Delta S_{\text{univ}} > 0$	$\Delta G < 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	$\Delta G > 0$	nonspontaneous
$\Delta S_{\text{univ}} = 0$	$\Delta G = 0$	reversible (at equilibrium)

. Willard Gibbs (1839–1903)

Born in Connecticut, Josiah Willard Gibbs attended Yale, as did his father, a professor of sacred literature at Yale, who was involved in the Amistad trial. In 1863, Gibbs was awarded the first engineering doctorate granted in the United States. He was appointed professor of mathematical physics at Yale in 1871, the first such professorship in the United States. His series of papers entitled "On the Equilibrium of Heterogeneous Substances" was the foundation of the field of physical chemistry and is considered one of the great achievements of the 19th century. Gibbs, whose work was translated into French by Le Chatelier, lived with his sister and brother-in-law until his death in 1903, shortly before the inauguration of the Nobel Prizes.

Gibbs energy is a state function, so its value depends only on the conditions of the initial and final states of the system that have undergone some change. A convenient and common approach to the calculation of free energy changes for physical and chemical reactions is by use of widely available compilations of standard state thermodynamic data. One method involves the use of standard enthalpies and entropies to compute standard free energy changes according to the following relation as demonstrated in Example 8.4.1.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{label}\{\{\backslash\text{PageIndex}\{7\}\}\}$$



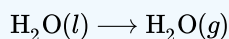
The Definition of Gibbs Free Energy: <https://youtu.be/iuWkcHUh-1o>

✓ Example 8.4.2: Evaluation of ΔG°

Change from ΔH° and ΔS° Use standard enthalpy and entropy data from Appendix G to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for ΔG° say about the spontaneity of this process?

Solution

The process of interest is the following:



The standard change in free energy may be calculated using the following equation:

$$\Delta G_{298}^\circ = \Delta H^\circ - T\Delta S^\circ$$

From Appendix G, here is the data:

Substance	ΔH_f° (kJ/mol)	S_{298}° (J/K·mol)
$\text{H}_2\text{O}(l)$	-286.83	70.0
$\text{H}_2\text{O}(g)$	-241.82	188.8

Combining at 298 K:

$$\begin{aligned}\Delta H^\circ &= \Delta H_{298}^\circ = \Delta H_f^\circ(\text{H}_2\text{O}(g)) - \Delta H_f^\circ(\text{H}_2\text{O}(l)) \\ &= [-241.82 \text{ kJ} - (-286.83)] \text{ kJ/mol} = 44.01 \text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \Delta S_{298}^\circ = S_{298}^\circ(\text{H}_2\text{O}(g)) - S_{298}^\circ(\text{H}_2\text{O}(l)) \\ &= 188.8 \text{ J/mol} \cdot \text{K} - 70.0 \text{ J/K} = 118.8 \text{ J/mol} \cdot \text{K}\end{aligned}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

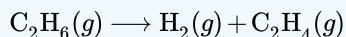
Converting everything into kJ and combining at 298 K:

$$\begin{aligned}\Delta G_{298}^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 44.01 \text{ kJ/mol} - (298 \text{ K} \times 118.8 \text{ J/mol} \cdot \text{K}) \times \frac{1 \text{ kJ}}{1000 \text{ J}} \\ &= 44.01 \text{ kJ/mol} - 35.4 \text{ kJ/mol} = 8.6 \text{ kJ/mol}\end{aligned}$$

At 298 K (25 °C) $\Delta G_{298}^{\circ} > 0$, and so boiling is nonspontaneous (not spontaneous).

? Exercise 8.4.2

Use standard enthalpy and entropy data from Appendix G to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for ΔG° say about the spontaneity of this process?



Answer:

$\Delta G_{298}^{\circ} = 102.0 \text{ kJ/mol}$; the reaction is nonspontaneous (not spontaneous) at 25 °C.

Free energy changes may also use the standard free energy of formation (ΔG_f°), for each of the reactants and products involved in the reaction. The standard free energy of formation is the free energy change that accompanies the formation of one mole of a substance from its elements in their standard states. Similar to the standard enthalpies of formation, (ΔG_f°) is by definition zero for elemental substances under standard state conditions. The approach to computing the free energy change for a reaction using this approach is the same as that demonstrated previously for enthalpy and entropy changes. For the reaction



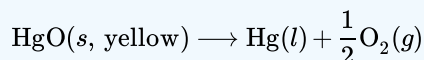
the standard free energy change at room temperature may be calculated as

$$\Delta G_{298}^{\circ} = \Delta G^{\circ} = \sum \nu \Delta G_{298}^{\circ}(\text{products}) - \sum \nu \Delta G_{298}^{\circ}(\text{reactants}) \quad (8.4.12)$$

$$= [x \Delta G_f^{\circ}(\text{C}) + y \Delta G_f^{\circ}(\text{D})] - [m \Delta G_f^{\circ}(\text{A}) + n \Delta G_f^{\circ}(\text{B})]. \quad (8.4.13)$$

✓ Example 8.4.3: Calculation of ΔG_{298}°

Consider the decomposition of yellow mercury(II) oxide.



Calculate the standard free energy change at room temperature, ΔG_{298}° , using (a) standard free energies of formation and (b) standard enthalpies of formation and standard entropies. Do the results indicate the reaction to be spontaneous or nonspontaneous under standard conditions?

Solution

The required data are available in [Appendix G](#) and are shown here.

Compound	ΔG_f° (kJ/mol)	ΔH_f° (kJ/mol)	S_{298}° (J/K·mol)
HgO (s, yellow)	-58.43	-90.46	71.13
Hg(l)	0	0	75.9
O ₂ (g)	0	0	205.2

(a) Using free energies of formation:

$$\begin{aligned} \Delta G_{298}^{\circ} &= \sum \nu \Delta G_{298}^{\circ}(\text{products}) - \sum \nu \Delta G_{298}^{\circ}(\text{reactants}) \\ &= \left[1 \Delta G_{298}^{\circ} \text{Hg}(l) + \frac{1}{2} \Delta G_{298}^{\circ} \text{O}_2(g) \right] - 1 \Delta G_{298}^{\circ} \text{HgO}(s, \text{yellow}) \\ &= \left[1 \text{ mol}(0 \text{ kJ/mol}) + \frac{1}{2} \text{ mol}(0 \text{ kJ/mol}) \right] - 1 \text{ mol}(-58.43 \text{ kJ/mol}) = 58.43 \text{ kJ/mol} \end{aligned}$$

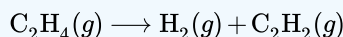
(b) Using enthalpies and entropies of formation:

$$\begin{aligned}
 \Delta H_{298}^{\circ} &= \sum \nu \Delta H_{298}^{\circ}(\text{products}) - \sum \nu \Delta H_{298}^{\circ}(\text{reactants}) \\
 &= \left[1 \Delta H_{298}^{\circ} \text{Hg}(l) + \frac{1}{2} \Delta H_{298}^{\circ} \text{O}_2(g) \right] - 1 \Delta H_{298}^{\circ} \text{HgO}(s, \text{yellow}) \\
 &= [1 \text{ mol}(0 \text{ kJ/mol}) + \frac{1}{2} \text{ mol}(0 \text{ kJ/mol})] - 1 \text{ mol}(-90.46 \text{ kJ/mol}) = 90.46 \text{ kJ/mol} \\
 \Delta S_{298}^{\circ} &= \sum \nu \Delta S_{298}^{\circ}(\text{products}) - \sum \nu \Delta S_{298}^{\circ}(\text{reactants}) \\
 &= \left[1 \Delta S_{298}^{\circ} \text{Hg}(l) + \frac{1}{2} \Delta S_{298}^{\circ} \text{O}_2(g) \right] - 1 \Delta S_{298}^{\circ} \text{HgO}(s, \text{yellow}) \\
 &= \left[1 \text{ mol}(75.9 \text{ J/mol K}) + \frac{1}{2} \text{ mol}(205.2 \text{ J/mol K}) \right] - 1 \text{ mol}(71.13 \text{ J/mol K}) = 107.4 \text{ J/mol K} \\
 \Delta G^{\circ} &= \Delta H^{\circ} - T \Delta S^{\circ} = 90.46 \text{ kJ} - 298.15 \text{ K} \times 107.4 \text{ J/K} \cdot \text{mol} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \\
 \Delta G^{\circ} &= (90.46 - 32.01) \text{ kJ/mol} = 58.45 \text{ kJ/mol}
 \end{aligned}$$

Both ways to calculate the standard free energy change at 25 °C give the same numerical value (to three significant figures), and both predict that the process is nonspontaneous (not spontaneous) at room temperature.

? Exercise 8.4.3

Calculate ΔG° using (a) free energies of formation and (b) enthalpies of formation and entropies (Appendix G). Do the results indicate the reaction to be spontaneous or nonspontaneous at 25 °C?



Answer

−141.5 kJ/mol, nonspontaneous

Key Concepts and 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. Gibbs free energy (G) is a state function defined with regard to system quantities only and may be used to predict the spontaneity of a process. A negative value for ΔG indicates a spontaneous process; a positive ΔG indicates a nonspontaneous process; and a ΔG of zero indicates that the system is at equilibrium. A number of approaches to the computation of free energy changes are possible.

Key Equations

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

Glossary

Gibbs free energy change (G)

thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in G

standard free energy change (ΔG°)

change in free energy for a process occurring under standard conditions (1 bar pressure for gases, 1 M concentration for solutions)

standard free energy of formation (ΔG_f°)

change in free energy accompanying the formation of one mole of substance from its elements in their standard states

second law of thermodynamics

entropy of the universe increases for a spontaneous process

standard entropy (S°)

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

standard entropy change (ΔS°)

change in entropy for a reaction calculated using the standard entropies, usually at room temperature and denoted ΔS_{298}°

Contributors and Attributions

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