

## 7.10: Gibbs Free Energy

### Skills to Develop

- To understand the relationship between the standard Gibbs free energy change, the extent of reaction, and equilibrium
- To understand the relationship between Gibbs free energy change and the direction in which a reaction will proceed to reach equilibrium
- To understand the relationship between Gibbs free energy and work.

### Gibbs Free-Energy

The Gibbs free energy ( $G$ ), often called simply free energy, was named in honor of J. Willard Gibbs (1838–1903), an American physicist who first developed the concept. It is defined in terms of three other state functions with which you are already familiar: enthalpy, temperature, and entropy:

$$G = H - TS \quad (7.10.1)$$

Because it is a combination of state functions,  $G$  is also a state function.

The relationship between the entropy change of the surroundings and the heat gained or lost by the system provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe.

### Standard Gibbs Free-Energy Change

We have seen that there is no way to measure absolute enthalpies, although we can measure changes in enthalpy ( $\Delta H$ ) during a chemical reaction. Because enthalpy is one of the components of Gibbs free energy, we are consequently unable to measure absolute free energies; we can measure only changes in free energy. The standard free-energy change ( $\Delta G^\circ$ ) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. This set of conditions required for determining  $\Delta G^\circ$  is rarely, if ever, encountered when carrying out chemical reactions, so the literal meaning of  $\Delta G^\circ$  is of questionable value. However, the **sign** and **magnitude** of  $\Delta G^\circ$  are extremely helpful in describing whether the reaction is product-favored or reactant-favored when it has reached equilibrium, which is sometimes known as the extent of a chemical reaction.

The standard free-energy change can be calculated from the definition of free energy, if the standard enthalpy and entropy changes are known, using Equation 7.10.2:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7.10.2)$$

- $\Delta G^\circ < 0$  means that the reaction is product-favored at equilibrium; the odds are in favor of making a significant amount of product at equilibrium.
- $\Delta G^\circ > 0$  means that the reaction is reactant-favored at equilibrium; the odds are against making a significant amount of product at equilibrium.

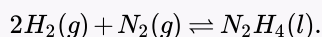
***It is important to recognize that a positive value of  $\Delta G^\circ$  for a reaction does not mean that no products will form if the reactants in their standard states are mixed; it means only that, at equilibrium, the concentrations of the products will be less than the concentrations of the reactants.***

- $\Delta G^\circ = 0$  means that the reaction is neither product-favored nor reactant-favored at equilibrium; there are 50:50 odds that a significant amount of product will be made at equilibrium.

**This situation is rare for chemical reactions, although it can happen.** This situation describes all phase changes when they occur at the exact phase change temperature.

### Exercise 7.10.1

Calculate the standard free-energy change ( $\Delta G^\circ$ ) at 25°C for the reaction



Is the reaction product-favored at equilibrium as written at 25°C?

#### Hint

At 25°C, the standard enthalpy change ( $\Delta H^\circ$ ) is 50.6 kJ/mol, and the standard entropy change ( $\Delta S^\circ$ ) is -0.332 kJ/(mol•K)

#### Answer

149.5 kJ/mol

no, not product-favored, but reactant-favored, at equilibrium

[Video Solution](#)

Calculated values of  $\Delta G^\circ$  are used to predict whether a reaction will be product-favored at equilibrium when the reactants and products are mixed under standard conditions. Very few reactions are actually carried out under standard conditions, and calculated values of  $\Delta G^\circ$  may not tell us whether a given reaction will occur spontaneously under nonstandard conditions. What determines whether a reaction will occur spontaneously is the free-energy change ( $\Delta G$ , notice the missing nought!) under the actual experimental conditions, which are usually quite different from  $\Delta G^\circ$ . Because  $\Delta H$  and  $\Delta S$  usually do not vary greatly with temperature in the absence of a phase change, we can use tabulated values of  $\Delta H^\circ$  and  $\Delta S^\circ$  to calculate  $\Delta G^\circ$  at various temperatures, as long as no phase change occurs over the temperature range being considered.

We can also use the signs of  $\Delta H^\circ$  and  $\Delta S^\circ$  to determine the **sign** of  $\Delta G^\circ$  for a given reaction at various temperatures. Using Equation 7.10.2, the sign of  $\Delta G^\circ$  can be predicted for a reaction, using the signs of  $\Delta H^\circ$  and  $\Delta S^\circ$ :

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7.10.3)$$

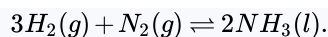
sign of $\Delta H^\circ$	sign of $\Delta S^\circ$	sign of $\Delta G^\circ$	Meaning
–	+	–	The reaction is product-favored at equilibrium at all temperatures; always likely; odds always favor it
+	–	+	The reaction is reactant-favored at equilibrium at all temperatures; never likely; odds are always against it
+	+	-/+	The <b>sign</b> of $\Delta G^\circ$ is temperature dependent. The reaction will be product-favored at relatively <b>high</b> temperatures.
–	–	-/+	The <b>sign</b> of $\Delta G^\circ$ is temperature dependent. The reaction will be product-favored at relatively <b>low</b> temperatures.

NOTE: If  $\Delta S^\circ$  and  $\Delta H^\circ$  for a reaction have the same sign, then the **sign** of  $\Delta G^\circ$  depends on the temperature and thus the relative magnitudes of the  $\Delta H^\circ$  and  $T\Delta S^\circ$  terms.

If  $\Delta S^\circ$  and  $\Delta H^\circ$  for a reaction have the same sign, then there is a specific temperature at which the sign of  $\Delta G^\circ$  must equal 0 as the reaction shifts from being reactant-favored at equilibrium to being product-favored at equilibrium, and vice versa. The temperature at which this flip over occurs, at which a given reaction is neither product-favored nor reactant-favored, can be calculated by setting  $\Delta G^\circ = 0$  in Equation 7.10.2 as illustrated in Example 7.10.2

#### Example 7.10.2

The reaction of nitrogen and hydrogen gas to produce ammonia



is one in which  $\Delta H^\circ$  is  $-91.8$  kJ and  $\Delta S^\circ$  is  $-198.1$  J/K (both are negative). Such reactions are predicted to be product-favored at low temperatures but reactant-favored at high temperatures.

Calculate the temperature at which this reaction changes from product-favored to reactant-favored, assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of temperature.

**Given:**  $\Delta H^\circ$  and  $\Delta S^\circ$

**Asked for:** temperature at which reaction changes from product-favored to reactant-favored

**Strategy:**

Set  $\Delta G^\circ$  equal to zero in Equation 7.10.2 and solve for T, the temperature at which the reaction becomes reactant-favored.

### SOLUTION

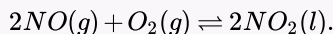
The temperature at which the reaction becomes reactant-favored at equilibrium is found by setting  $\Delta G^\circ$  equal to zero and rearranging Equation 7.10.2 to solve for T:

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = 0 \\ \Delta H^\circ &= T\Delta S^\circ \\ T &= \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{(-91.8 \text{ kJ})(1000 \text{ J/kJ})}{-198.1 \text{ J/K}} = 463 \text{ K}\end{aligned}$$

This is a case in which a chemical engineer is severely limited by thermodynamics. Any attempt to increase the rate of reaction of nitrogen with hydrogen by increasing the temperature will cause reactants to be favored over products above 463 K.

### Exercise 7.10.2

$\Delta H^\circ = -116.2$  kJ and  $\Delta S^\circ = -146.6$  J/K for the reaction of nitric oxide and oxygen to form nitrogen dioxide.



Use those data to calculate the temperature at which this reaction changes from product-favored to reactant-favored.

**Answer**

792.6 K

[Video Solution](#)

## Gibbs Free Energy and the Direction of Spontaneous Reactions

A second major goal of chemical thermodynamics is to establish criteria for predicting whether a particular reaction or process will occur spontaneously, that is, if it will proceed in the forward direction, as written, to reach equilibrium. We have developed one such criterion, the change in entropy of the universe: if  $\Delta S_{\text{univ}} > 0$  for a process or a reaction, then the process will go in the forward direction as written to reach equilibrium. Conversely, if  $\Delta S_{\text{univ}} < 0$ , a process will go in the reverse direction as written to reach equilibrium; if  $\Delta S_{\text{univ}} = 0$ , the system is already at equilibrium. The sign of  $\Delta S_{\text{univ}}$  is a universally applicable and infallible indicator of the direction of a reaction as it proceeds towards equilibrium. Unfortunately, using  $\Delta S_{\text{univ}}$  requires that we calculate  $\Delta S$  for both a system and its surroundings. This calculation is not particularly useful for two reasons: we are normally much more interested in the system than in the surroundings, and it is difficult to make quantitative measurements of the surroundings (i.e., the rest of the universe). A criterion of spontaneity that is based solely on the state functions of a system would be much more convenient, and is provided by the Gibbs free energy.

The criterion for predicting the likely direction for the reaction to occur to reach equilibrium is based on ( $\Delta G$ ), the change in  $G$ , at constant temperature and pressure. Although very few chemical reactions actually occur under conditions of constant temperature and pressure, most systems can be brought back to the initial temperature and pressure without significantly affecting the value of thermodynamic state functions such as  $G$ . At constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S \quad (7.10.4)$$

where all thermodynamic quantities are those of the system.

The relationship between the entropy change of the surroundings and the heat gained or lost by the system provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe. The relationship shown in Equation 7.10.4 allows us to predict spontaneity by focusing exclusively on the thermodynamic properties and temperature of the system. We predict that highly exothermic processes ( $\Delta H \ll 0$ ) that increase the disorder of a system ( $\Delta S_{sys} \gg 0$ ) would therefore occur spontaneously. An example of such a process is the decomposition of ammonium nitrate fertilizer. Ammonium nitrate was also used to destroy the Murrah Federal Building in Oklahoma City, Oklahoma, in 1995.

For a system at constant temperature and pressure, we can summarize the following results:

- If  $\Delta G < 0$ , the process occurs spontaneously, that is, it proceeds in the forward direction, as written, until it reaches equilibrium.
- If  $\Delta G = 0$ , the system is at equilibrium.
- If  $\Delta G > 0$ , the process is not spontaneous as written but occurs spontaneously in the reverse direction, until it reaches equilibrium.

To further understand how the various components of  $\Delta G$  dictate whether a process occurs spontaneously, we now look at a simple and familiar physical change: the conversion of liquid water to water vapor. If this process is carried out at 1 atm and the normal boiling point of 100.00°C (373.15 K), we can calculate  $\Delta G$  from the experimentally measured value of  $\Delta H_{vap}$  (40.657 kJ/mol). For vaporizing 1 mol of water,  $\Delta H = 40,657 \text{ J}$ , so the process is highly endothermic. The value of  $\Delta S$  is 108.96 J/K

Hence there is an increase in the disorder of the system. At the normal boiling point of water,

$$\begin{aligned} \Delta G_{100^\circ\text{C}} &= \Delta H_{100^\circ\text{C}} - T\Delta S_{100^\circ\text{C}} \\ &= 40,657 \text{ J} - [(373.15 \text{ K})(108.96 \text{ J/K})] \\ &= 0 \text{ J} \end{aligned}$$

The energy required for vaporization offsets the increase in disorder of the system. Thus  $\Delta G = 0$ , and the liquid and vapor are in equilibrium, as is true of any liquid at its boiling point under standard conditions.

Now suppose we were to superheat 1 mol of liquid water to 110°C. The value of  $\Delta G$  for the vaporization of 1 mol of water at 110°C, assuming that  $\Delta H$  and  $\Delta S$  do not change significantly with temperature, becomes

$$\begin{aligned} \Delta G_{110^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40,657 \text{ J} - [(383.15 \text{ K})(108.96 \text{ J/K})] \\ &= -1091 \text{ J} \end{aligned}$$

At 110°C,  $\Delta G < 0$ , and vaporization is predicted to occur spontaneously and irreversibly.

We can also calculate  $\Delta G$  for the vaporization of 1 mol of water at a temperature below its normal boiling point—for example, 90°C—making the same assumptions:

$$\begin{aligned} \Delta G_{90^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40,657 \text{ J} - [(363.15 \text{ K})(108.96 \text{ J/K})] \\ &= 1088 \text{ J} \end{aligned}$$

At 90°C,  $\Delta G > 0$ , and water does not spontaneously convert to water vapor. When using all the digits in the calculator display in carrying out our calculations,  $\Delta G_{110^\circ\text{C}} = 1090 \text{ J} = -\Delta G_{90^\circ\text{C}}$ , as we would predict.

#### Relating Enthalpy and Entropy changes under Equilibrium Conditions

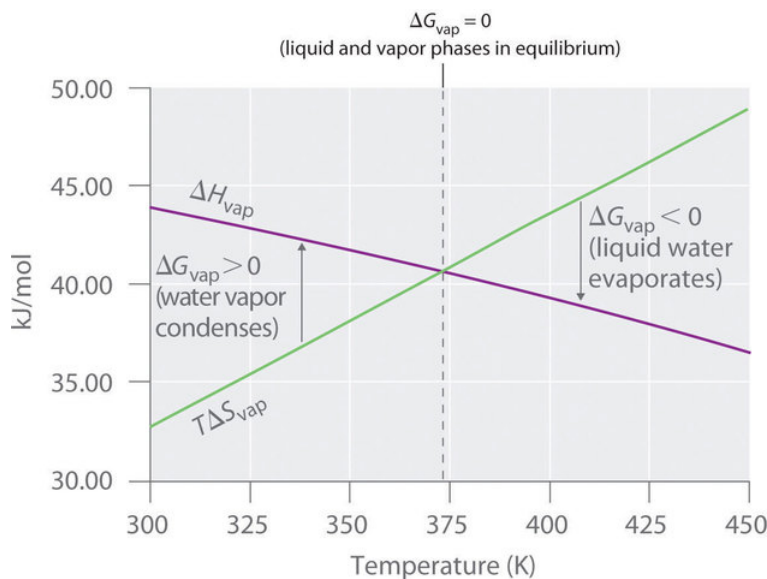
$\Delta G = 0$  only if  $\Delta H = T\Delta S$ .

We can also calculate the temperature at which liquid water is in equilibrium with water vapor. Inserting the values of  $\Delta H$  and  $\Delta S$  into the definition of  $\Delta G$  (Equation 7.10.2), setting  $\Delta G = 0$ , and solving for  $T$ ,

$$0 \text{ J} = 40,657 \text{ J} - T(108.96 \text{ J/K})$$

$$T = 373.15 \text{ K}$$

Thus  $\Delta G = 0$  at  $T = 373.15 \text{ K}$  and 1 atm, which indicates that liquid water and water vapor are in equilibrium; this temperature is called the normal boiling point of water. At temperatures greater than 373.15 K,  $\Delta G$  is negative, and water evaporates spontaneously and irreversibly. Below 373.15 K,  $\Delta G$  is positive, and water does not evaporate spontaneously. Instead, water vapor at a temperature less than 373.15 K and 1 atm will spontaneously and irreversibly condense to liquid water. Figure 7.10.1 shows how the  $\Delta H$  and  $T\Delta S$  terms vary with temperature for the vaporization of water. When the two lines cross,  $\Delta G = 0$ , and  $\Delta H = T\Delta S$ .



**Figure 7.10.1:** Temperature Dependence of  $\Delta H$  and  $T\Delta S$  for the Vaporization of Water. Both  $\Delta H$  and  $T\Delta S$  are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where  $\Delta H = T\Delta S$ . Because  $\Delta G = \Delta H - T\Delta S$ , at this temperature  $\Delta G = 0$ , indicating that the liquid and vapor phases are in equilibrium. The normal boiling point of water is therefore 373.15 K. Above the normal boiling point, the  $T\Delta S$  term is greater than  $\Delta H$ , making  $\Delta G < 0$ ; hence, liquid water evaporates spontaneously. Below the normal boiling point, the  $\Delta H$  term is greater than  $T\Delta S$ , making  $\Delta G > 0$ . Thus liquid water does not evaporate spontaneously, but water vapor spontaneously condenses to liquid.

## The Relationship between $\Delta G$ and Work

In the previous subsection, we learned that the value of  $\Delta G$  allows us to predict the spontaneity of a physical or a chemical change. In addition, the **magnitude** of  $\Delta G$  for a process provides other important information. The change in free energy ( $\Delta G$ ) is equal to the maximum amount of work that a system can perform on the surroundings while undergoing a spontaneous change (at constant temperature and pressure):  $\Delta G = w_{\text{max}}$ . To see why this is true, let's look again at the relationships among free energy, enthalpy, and entropy expressed in Equation 7.10.2. We can rearrange this equation as follows:

$$\Delta H = \Delta G + T\Delta S \quad (7.10.5)$$

This equation tells us that when energy is released during an exothermic process ( $\Delta H < 0$ ), such as during the combustion of a fuel, some of that energy can be used to do work ( $\Delta G < 0$ ), while some is used to increase the entropy of the universe ( $T\Delta S > 0$ ). Only if the process occurs infinitely slowly in a perfectly reversible manner will the entropy of the universe be unchanged. (For more information on entropy and reversibility, see the previous section). Because no real system is perfectly reversible, the entropy of the universe increases during all processes that produce energy. As a result, no process that uses stored energy can ever be 100% efficient; that is,  $\Delta H$  will never equal  $\Delta G$  because  $\Delta S$  has a positive value.

One of the major challenges facing engineers is to maximize the efficiency of converting stored energy to useful work or converting one form of energy to another. As indicated in Table 7.10.1, the efficiencies of various energy-converting devices vary

widely. For example, an internal combustion engine typically uses only 25%–30% of the energy stored in the hydrocarbon fuel to perform work; the rest of the stored energy is released in an unusable form as heat. In contrast, gas–electric hybrid engines, now used in several models of automobiles, deliver approximately 50% greater fuel efficiency. A large electrical generator is highly efficient (approximately 99%) in converting mechanical to electrical energy, but a typical incandescent light bulb is one of the least efficient devices known (only approximately 5% of the electrical energy is converted to light). In contrast, a mammalian liver cell is a relatively efficient machine and can use fuels such as glucose with an efficiency of 30%–50%.

**Table 7.10.1:** Approximate Thermodynamic Efficiencies of Various Devices

Device	Energy Conversion	Approximate Efficiency (%)
large electrical generator	mechanical → electrical	99
chemical battery	chemical → electrical	90
home furnace	chemical → heat	65
small electric tool	electrical → mechanical	60
space shuttle engine	chemical → mechanical	50
mammalian liver cell	chemical → chemical	30–50
spinach leaf cell	light → chemical	30
internal combustion engine	chemical → mechanical	25–30
fluorescent light	electrical → light	20
solar cell	light → electricity	10–20
incandescent light bulb	electricity → light	5
yeast cell	chemical → chemical	2–4

## Summary

- The change in Gibbs free energy, which is based solely on changes in state functions, is the criterion for describing two aspects of a reaction.
- Standard free-energy change:

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

The standard free-energy change ( $\Delta G^{\circ}$ ) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The sign of  $\Delta G^{\circ}$  tells us if a reaction will be reactant-favored (+  $\Delta G^{\circ}$ ) or product-favored (−  $\Delta G^{\circ}$ ) at equilibrium. The magnitude of  $\Delta G^{\circ}$  tells us the extent of the reaction. A large + $\Delta G^{\circ}$  tells us the reaction makes very little product at equilibrium. A large −  $\Delta G^{\circ}$  tells us the reaction makes a great deal of product at equilibrium.

- Free-energy change:

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

The change in free energy ( $\Delta G$ ) is the difference between the heat released during a process and the heat released for the same process occurring in a reversible manner. If a system is at equilibrium,  $\Delta G = 0$ . If the process is spontaneous,  $\Delta G < 0$ . If the process is not spontaneous as written, but is spontaneous in the reverse direction,  $\Delta G > 0$ . At constant temperature and pressure,  $\Delta G$  is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change.

## Contributors

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