

18.6: Gibbs Free Energy

Equation 18.2 establishes a relationship between the enthalpy change in a system and the entropy change in the surroundings. Recall that for any process the entropy change of the universe is the sum of the entropy change of the system and the entropy change of the surroundings:

[18.3]

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

Recall also that ΔS_{univ} is the criterion for spontaneity. A positive ΔS_{univ} indicates a spontaneous process, and a negative ΔS_{univ} indicates a nonspontaneous process. In this section, we derive a new thermodynamic function called Gibbs free energy, which, like ΔS_{univ} , is a criterion for spontaneity. However, Gibbs free energy focuses entirely on the system.

Defining Gibbs Free Energy

Combining **Equation 18.3** with **Equation 18.2** gives us the following relationship at constant temperature and pressure:

[18.4]

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T}$$

Using **Equation 18.4**, we can calculate ΔS_{univ} while focusing only on the *system*. If we multiply **Equation 18.4** by $-T$ we arrive at the expression:

[18.5]

$$\begin{aligned} -T\Delta S_{\text{univ}} &= -T\Delta S_{\text{sys}} + \cancel{T} \frac{\Delta H_{\text{sys}}}{\cancel{T}} \\ &= \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} \end{aligned}$$

If we drop the subscript *sys*—from now on ΔH and ΔS without subscripts mean ΔH_{sys} and ΔS_{sys} —we get the expression:

[18.6]

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S$$

The right-hand side of **Equation 18.6** represents the change in *Gibbs free energy*. The formal definition of **Gibbs free energy (G)** is:

[18.7]

$$G = H - TS$$

where H is enthalpy, T is the temperature in kelvins, and S is entropy. The *change* in Gibbs free energy, symbolized by ΔG , is expressed as follows (at constant temperature):

[18.8]

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

If we combine [Equations 18.6](#) and [18.8](#), we have an equation that makes clear the significance of ΔG :

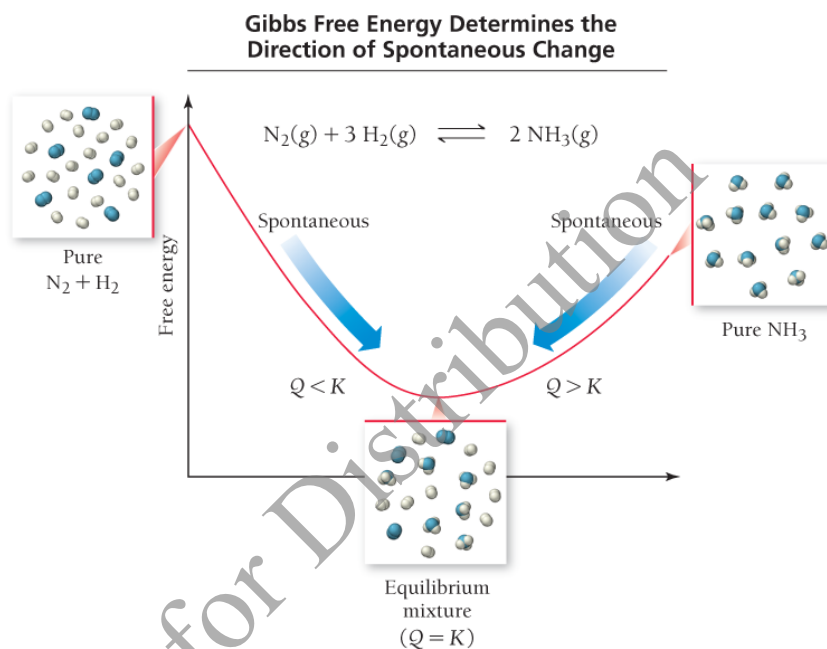
[18.9]

$$\Delta G = -T\Delta S_{\text{univ}} \quad (\text{constant } T, P)$$

The change in Gibbs free energy for a process occurring at constant temperature and pressure is proportional to the negative of ΔS_{univ} . Since ΔS_{univ} is a criterion for spontaneity, ΔG is also a criterion for spontaneity (although opposite in sign). In fact, Gibbs free energy is also called *chemical potential* because it is analogous to mechanical potential energy discussed earlier. Just as mechanical systems tend toward lower potential energy, so chemical systems tend toward lower Gibbs free energy (toward lower chemical potential) ([Figure 18.4](#)).

Figure 18.4 Gibbs Free Energy

Gibbs free energy is also called chemical potential because it determines the direction of spontaneous change for chemical systems.



Summarizing Gibbs Free Energy (at Constant Temperature and Pressure):

- ΔG is proportional to the negative of ΔS_{univ} .
- A decrease in Gibbs free energy ($\Delta G < 0$) corresponds to a spontaneous process.
- An increase in Gibbs free energy ($\Delta G > 0$) corresponds to a nonspontaneous process.

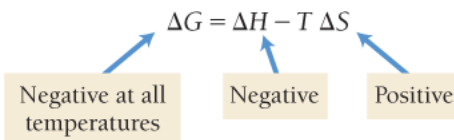
Notice that we can calculate changes in Gibbs free energy solely with reference to the system. So, to determine whether a process is spontaneous, we only have to find the change in *entropy* for the system (ΔS) and the change in *enthalpy* for the system (ΔH). We can then predict the spontaneity of the process at any temperature. In [Chapter 9](#) we learned how to calculate changes in enthalpy (ΔH) for chemical reactions. In [Section 18.7](#), we will learn how to calculate changes in entropy (ΔS) for chemical reactions. We can then use those two quantities to calculate changes in free energy (ΔG) for chemical reactions and predict their spontaneity. Before we move on to doing this, however, we examine some examples that demonstrate how ΔH , ΔS , and T affect the spontaneity of chemical processes.

The Effect of ΔH , ΔS , and T on Spontaneity

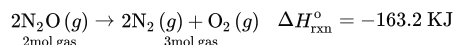
Key Concept Video The Effect of ΔH , ΔS , and T on Reaction Spontaneity

Case 1: ΔH Negative, ΔS Positive

If a reaction is exothermic ($\Delta H < 0$), and if the change in entropy for the reaction is positive ($\Delta S > 0$), then the change in free energy is negative at all temperatures and the reaction is spontaneous at all temperatures.



As an example, consider the dissociation of N_2O :

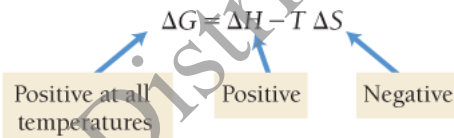


The change in *enthalpy* is negative—heat is emitted, increasing the entropy of the surroundings. The change in *entropy* for the reaction is positive, which means that the entropy of the system increases. (We can see that the change in entropy is positive from the balanced equation—the number of moles of gas increases.) Since the entropy of both the system and the surroundings increases, the entropy of the universe must also increase, making the reaction spontaneous at all temperatures.

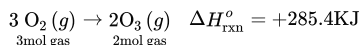
Recall from Chapter 9 that ΔH° represents the standard enthalpy change. The definition of the standard state was first given in Section 9.10 and is restated in Section 18.7.

Case 2: ΔH Positive, ΔS Negative

If a reaction is endothermic ($\Delta H > 0$), and if the change in entropy for the reaction is negative ($\Delta S < 0$), then the change in free energy is positive at all temperatures and the reaction is nonspontaneous at all temperatures.



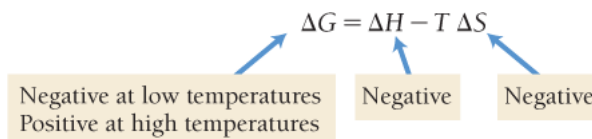
As an example, consider the formation of ozone from oxygen:



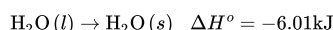
The change in *enthalpy* is positive—heat is therefore absorbed, *decreasing* the entropy of the surroundings. The change in *entropy* is negative, which means that the entropy of the system decreases. (We can see that the change in entropy is negative from the balanced equation—the number of moles of gas decreases.) Since the entropy of both the system and the surroundings decreases, the entropy of the universe must also decrease, making the reaction nonspontaneous at all temperatures.

Case 3: ΔH Negative, ΔS Negative

If a reaction is exothermic ($\Delta H < 0$) and if the change in entropy for the reaction is negative ($\Delta S < 0$), then the sign of the change in free energy depends on temperature. The reaction is spontaneous at low temperature but nonspontaneous at high temperature.



As an example, consider the freezing of liquid water to form ice:

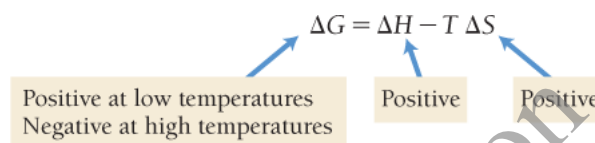


The change in *enthalpy* is negative—heat is emitted, increasing the entropy of the surroundings. The change in *entropy* is negative, which means that the entropy of the system decreases. (We can see that the change in entropy is negative from the balanced equation—a liquid turns into a solid.)

Unlike the two previous cases, where the changes in *entropy* of the system and of the surroundings had the same sign, the changes here are opposite in sign. Therefore, the sign of the change in free energy depends on the relative magnitudes of the two changes. At a low enough temperature, the heat emitted into the surroundings causes a large entropy change in the surroundings, making the process spontaneous. At high temperature, the same amount of heat is dispersed into warmer surroundings, so the positive entropy change in the surroundings is smaller, resulting in a nonspontaneous process.

Case 4: ΔH Positive, ΔS Positive

If a reaction is endothermic ($\Delta H > 0$) and if the change in entropy for the reaction is positive ($\Delta S > 0$), then the sign of the change in free energy again depends on temperature. The reaction is nonspontaneous at low temperature but spontaneous at high temperature.



As an example, consider the vaporizing of liquid water to gaseous water:



The change in *enthalpy* is positive—heat is absorbed from the surroundings, so the entropy of the surroundings decreases. The change in *entropy* is positive, which means that the entropy of the system increases. (We can see that the change in entropy is positive from the balanced equation—a liquid turns into a gas.) The changes in entropy of the system and the surroundings again have opposite signs, only this time the entropy of the surroundings decreases while the entropy of the system increases. In cases such as this, high temperature favors spontaneity because the absorption of heat from the surroundings has less effect on the entropy of the surroundings as temperature increases.

The results of this section are summarized in Table 18.1. Notice that when ΔH and ΔS have opposite signs, the spontaneity of the reaction does not depend on temperature. When ΔH and ΔS have the same sign, however, the spontaneity does depend on temperature. The temperature at which the reaction changes from being spontaneous to being nonspontaneous (or vice versa) is the temperature at which ΔG changes sign, which we can determine by setting $\Delta G = 0$ and solving for T , as shown in part b of Example 18.4.

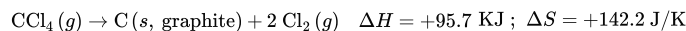
Table 18.1 The Effect of ΔH , ΔS , and T on Spontaneity

ΔH	ΔS	Low Temperature	High Temperature	Example
–	+	Spontaneous ($\Delta G < 0$)	Spontaneous ($\Delta G < 0$)	$2 \text{ N}_2\text{O}(g) \longrightarrow 2 \text{ N}_2(g) + \text{O}_2(g)$
+	–	Nonspontaneous ($\Delta G > 0$)	Nonspontaneous ($\Delta G > 0$)	$3 \text{ O}_2(g) \longrightarrow 2 \text{ O}_3(g)$
–	–	Spontaneous ($\Delta G < 0$)	Nonspontaneous ($\Delta G > 0$)	$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(s)$
+	+	Nonspontaneous ($\Delta G > 0$)	Spontaneous ($\Delta G < 0$)	$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$

Example 18.4 Calculating Gibbs Free Energy Changes and Predicting

Spontaneity from ΔH and ΔS

Consider the reaction for the decomposition of carbon tetrachloride gas:



- Calculate ΔG at 25 °C and determine whether the reaction is spontaneous.
- If the reaction is not spontaneous at 25 °C, determine at what temperature (if any) the reaction becomes spontaneous.

SOLUTION

- Use Equation 18.8 to calculate ΔG from the given values of ΔH and ΔS . The temperature must be in kelvins. Be sure to express both ΔH and ΔS in the same units (usually joules).

$$\begin{aligned} T &= 273 + 25 = 298\text{K} \\ \Delta G &= \Delta H - T\Delta S \\ &= 95.7 \times 10^3 \text{ J} - (298 \text{ K}) 142.2 \text{ J/K} \\ &= 95.7 \times 10^3 \text{ J} - 42.4 \times 10^3 \text{ J} \\ &= +53.3 \times 10^3 \text{ J} \end{aligned}$$

The reaction is not spontaneous.

- Since ΔS is positive, ΔG becomes more negative with increasing temperature. To determine the temperature at which the reaction becomes spontaneous, use Equation 18.8 to find the temperature at which ΔG changes from positive to negative (set $\Delta G = 0$ and solve for T). The reaction is spontaneous above this temperature.

$$\begin{aligned} \Delta G &= \Delta H - T\Delta S \\ 0 &= 95.7 \times 10^3 \text{ J} - (T) 142.2 \text{ J/K} \\ T &= \frac{95.7 \times 10^3 \text{ J}}{142.2 \text{ J/K}} \\ &= 673\text{K} \end{aligned}$$

FOR PRACTICE 18.4 Consider the reaction:



Calculate ΔG at 25 °C and determine whether the reaction is spontaneous. Does ΔG become more negative or more positive as the temperature increases?

Interactive Worked Example 18.4 Calculating Gibbs Free Energy Changes and Predicting Spontaneity from ΔH and ΔS

Conceptual Connection 18.3 ΔH , ΔS , and ΔG

Interactive

Not for Distribution

Not for Distribution

Not for Distribution