

## 14.7: Reaction Directions (Thermodynamic Explanation)

### Learning Objectives

- To know the relationship between free energy and the equilibrium constant.

We have identified three criteria for whether a given reaction will occur spontaneously:

- $\Delta S_{univ} > 0$  (2nd law of thermodynamics),
- $\Delta G_{sys} < 0$  (Gibbs Energy version), and
- the relative magnitude of the [reaction quotient](#)  $Q$  versus the equilibrium constant  $K$ .

Recall that if  $Q < K$ , then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if  $Q > K$ , then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If  $Q = K$ , then the system is at equilibrium, and no net reaction occurs. Table 14.7.1 summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes.

Table 14.7.1: Criteria for the Spontaneity of a Process as Written

| Spontaneous                            | Equilibrium           | Nonspontaneous*       |
|--|-----------------------|-----------------------|
| $\Delta S_{univ} > 0$                  | $\Delta S_{univ} = 0$ | $\Delta S_{univ} < 0$ |
| $\Delta G_{sys} < 0$                   | $\Delta G_{sys} = 0$  | $\Delta G_{sys} > 0$  |
| $Q < K$                                | $Q = K$               | $Q > K$               |
| *Spontaneous in the reverse direction. |                       |                       |

Because all three criteria assess the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. In this section, we explore the relationship between the standard free energy of reaction ( $\Delta G^\circ$ ) and the equilibrium constant ( $K$ ).

### Free Energy and the Equilibrium Constant

Because  $\Delta H^\circ$  and  $\Delta S^\circ$  determine the magnitude of  $\Delta G^\circ$  and because  $K$  is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express  $K$  in terms of  $\Delta G^\circ$  and vice versa. "Free Energy",  $\Delta G$  is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature, thereby eliminating  $\Delta H$  from the equation for  $\Delta G$ . The general relationship can be shown as follow (derivation not shown):

$$\Delta G = V\Delta P - S\Delta T \quad (14.7.1)$$

If a reaction is carried out at constant temperature ( $\Delta T = 0$ ), then Equation 14.7.1 simplifies to

$$\Delta G = V\Delta P \quad (14.7.2)$$

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. For reactions that involve gases, however, the effect of pressure on free energy is very important.

Assuming ideal gas behavior, we can replace the  $V$  in Equation 14.7.2 by  $nRT/P$  (where  $n$  is the number of moles of gas and  $R$  is the ideal gas constant) and express  $\Delta G$  in terms of the initial and final pressures ( $P_i$  and  $P_f$ , respectively):

$$\Delta G = \left( \frac{nRT}{P} \right) \Delta P \quad (14.7.3)$$

$$= nRT \frac{\Delta P}{P} = nRT \ln \left( \frac{P_f}{P_i} \right) \quad (14.7.4)$$

If the initial state is the standard state with  $P_i = 1$  atm, then the change in free energy of a substance when going from the standard state to any other state with a pressure  $P$  can be written as follows:

$$G - G^\circ = nRT \ln P \quad (14.7.5)$$

This can be rearranged as follows:

$$G = G^\circ + nRT \ln P \quad (14.7.6)$$

As you will soon discover, Equation 14.7.6 allows us to relate  $\Delta G^\circ$  and  $K_p$ . Any relationship that is true for  $K_p$  must also be true for  $K$  because  $K_p$  and  $K$  are simply different ways of expressing the equilibrium constant using different units.

Let's consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:



Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for  $\Delta G$ :

$$\Delta G = \sum_m G_{products} - \sum_n G_{reactants} \quad (14.7.8)$$

$$= (cG_C + dG_D) - (aG_A + bG_B) \quad (14.7.9)$$

Substituting Equation 14.7.6 for each term into Equation 14.7.9

$$\Delta G = [(cG_C^\circ + cRT \ln P_C) + (dG_D^\circ + dRT \ln P_D)] - [(aG_A^\circ + aRT \ln P_A) + (bG_B^\circ + bRT \ln P_B)] \quad (14.7.10)$$

Combining terms gives the following relationship between  $\Delta G$  and the reaction quotient  $Q$ :

$$\Delta G = \Delta G^\circ + RT \ln \left( \frac{P_C^c P_D^d}{P_A^a P_B^b} \right) \quad (14.7.11)$$

$$= \Delta G^\circ + RT \ln Q \quad (14.7.12)$$

where  $\Delta G^\circ$  indicates that all reactants and products are in their standard states. For gases at equilibrium ( $Q = K_p$ ), and as you've learned in this chapter,  $\Delta G = 0$  for a system at equilibrium. Therefore, we can describe the relationship between  $\Delta G^\circ$  and  $K_p$  for gases as follows:

$$0 = \Delta G^\circ + RT \ln K_p \quad (14.7.13)$$

$$\Delta G^\circ = -RT \ln K_p \quad (14.7.14)$$

If the products and reactants are in their standard states and  $\Delta G^\circ < 0$ , then  $K_p > 1$ , and products are favored over reactants. Conversely, if  $\Delta G^\circ > 0$ , then  $K_p < 1$ , and reactants are favored over products. If  $\Delta G^\circ = 0$ , then  $K_p = 1$ , and neither reactants nor products are favored: the system is at equilibrium.

**For a spontaneous process under standard conditions,  $K_{eq}$  and  $K_p$  are greater than 1.**

To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy change versus the extent of the reaction (for example, as reflected in the value of  $Q$ ), equilibrium is established when the system's free energy is minimized (Figure 14.7.3). If a system is present with reactants and products present in nonequilibrium amounts ( $Q \neq K$ ), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.

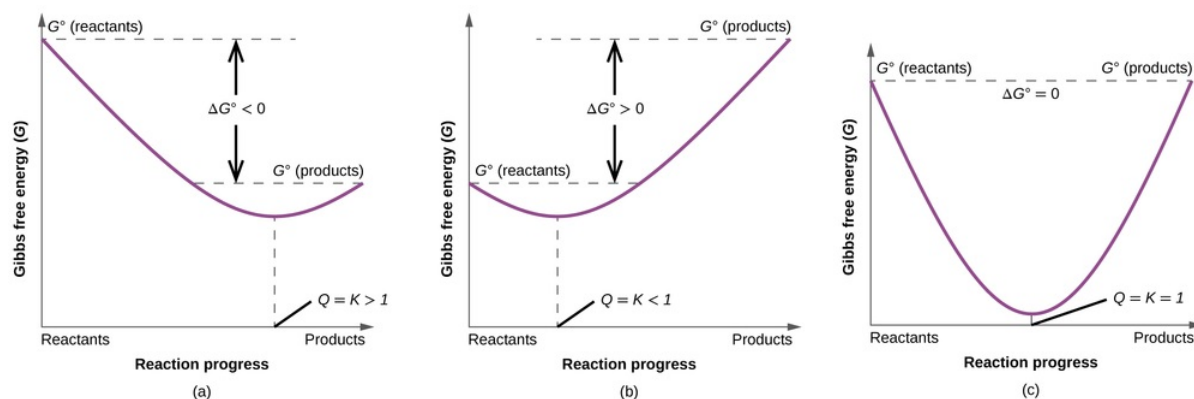
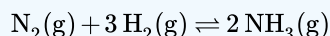


Figure 14.7.1: These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium. (CC BY 4.0; OpenStax).

### ✓ Example 14.7.2

$\Delta G^\circ$  is  $-32.7$  kJ/mol of  $N_2$  for the reaction



This calculation was for the reaction under standard conditions—that is, with all gases present at a partial pressure of 1 atm and a temperature of  $25^\circ\text{C}$ . Calculate  $\Delta G$  for the same reaction under the following nonstandard conditions:

- $P_{N_2} = 2.00$  atm,
- $P_{H_2} = 7.00$  atm,
- $P_{NH_3} = 0.021$  atm,
- and  $T = 100^\circ\text{C}$ .

Does the reaction favor products or reactants?

**Given:** balanced chemical equation, partial pressure of each species, temperature, and  $\Delta G^\circ$

**Asked for:** whether products or reactants are favored

**Strategy:**

- Using the values given and Equation 14.7.12 calculate  $Q$ .
- Substitute the values of  $\Delta G^\circ$  and  $Q$  into Equation 14.7.12 to obtain  $\Delta G$  for the reaction under nonstandard conditions.

**Solution:**

A The relationship between  $\Delta G^\circ$  and  $\Delta G$  under nonstandard conditions is given in Equation 14.7.12. Substituting the partial pressures given, we can calculate  $Q$ :

$$Q = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} = \frac{(0.021)^2}{(2.00)(7.00)^3} = 6.4 \times 10^{-7}$$

B Substituting the values of  $\Delta G^\circ$  and  $Q$  into Equation 14.7.12

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln Q \\ &= -32.7 \text{ kJ} + \left[ (8.314 \text{ J/K})(373 \text{ K}) \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right) \ln(6.4 \times 10^{-7}) \right] \\ &= -32.7 \text{ kJ} + (-44 \text{ kJ}) \\ &= -77 \text{ kJ/mol of } N_2 \end{aligned}$$

Because  $\Delta G < 0$  and  $Q < 1.0$ , the reaction is spontaneous to the right as written, so products are favored over reactants.

### ? Exercise 14.7.2

Calculate  $\Delta G$  for the reaction of nitric oxide with oxygen to give nitrogen dioxide under these conditions:  $T = 50^\circ\text{C}$ ,  $P_{\text{NO}} = 0.0100 \text{ atm}$ ,  $P_{\text{O}_2} = 0.200 \text{ atm}$ , and  $P_{\text{NO}_2} = 1.00 \times 10^{-4} \text{ atm}$ . The value of  $\Delta G^\circ$  for this reaction is  $-72.5 \text{ kJ/mol}$  of  $\text{O}_2$ . Are products or reactants favored?

#### Answer

$-92.9 \text{ kJ/mol}$  of  $\text{O}_2$ ; the reaction is spontaneous to the right as written, so products are favored.

### ✓ Example 14.7.3

Calculate  $K_p$  for the reaction of  $\text{H}_2$  with  $\text{N}_2$  to give  $\text{NH}_3$  at  $25^\circ\text{C}$ .  $\Delta G^\circ$  for this reaction is  $-32.7 \text{ kJ/mol}$  of  $\text{N}_2$ .

**Given:** balanced chemical equation from Example 14.7.2  $\Delta G^\circ$ , and temperature

**Asked for:**  $K_p$

**Strategy:**

Substitute values for  $\Delta G^\circ$  and  $T$  (in kelvin) into Equation 14.7.14 to calculate  $K_p$ , the equilibrium constant for the formation of ammonia.

#### Solution

In Example 10, we used tabulated values of  $\Delta G^\circ_f$  to calculate  $\Delta G^\circ$  for this reaction ( $-32.7 \text{ kJ/mol}$  of  $\text{N}_2$ ). For equilibrium conditions, rearranging Equation 14.7.14

$$\begin{aligned}\Delta G^\circ &= -RT \ln K_p \\ \frac{-\Delta G^\circ}{RT} &= \ln K_p\end{aligned}$$

Inserting the value of  $\Delta G^\circ$  and the temperature ( $25^\circ\text{C} = 298 \text{ K}$ ) into this equation,

$$\begin{aligned}\ln K_p &= -\frac{(-32.7 \text{ kJ})(1000 \text{ J/kJ})}{(8.314 \text{ J/K})(298 \text{ K})} = 13.2 \\ K_p &= 5.4 \times 10^5\end{aligned}$$

Thus the equilibrium constant for the formation of ammonia at room temperature is favorable. However, the rate at which the reaction occurs at room temperature is too slow to be useful.

### ? Exercise 14.7.3

Calculate  $K_p$  for the reaction of  $\text{NO}$  with  $\text{O}_2$  to give  $\text{NO}_2$  at  $25^\circ\text{C}$ .  $\Delta G^\circ$  for this reaction is  $-70.5 \text{ kJ/mol}$  of  $\text{O}_2$ .

#### Answer

$2.2 \times 10^{12}$

Although  $K_p$  is defined in terms of the partial pressures of the reactants and the products, the equilibrium constant  $K$  is defined in terms of the concentrations of the reactants and the products. We described the relationship between the numerical magnitude of  $(K_{-p})$  and  $K$  previously and showed that they are related:

$$K_p = K(RT)^{\Delta n} \quad (14.7.15)$$

where  $\Delta n$  is the number of moles of gaseous product minus the number of moles of gaseous reactant. For reactions that involve only solutions, liquids, and solids,  $\Delta n = 0$ , so  $K_p = K$ . For all reactions that do not involve a change in the number of moles of gas present, the relationship in Equation 14.7.14 can be written in a more general form:

$$\Delta G^\circ = -RT \ln K \quad (14.7.16)$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 14.7.16 for the difference between  $K_p$  and  $K$ . Although we typically use concentrations or pressures in our equilibrium calculations, recall that equilibrium constants are generally expressed as unitless numbers because of the use of **activities** or **fugacities** in precise thermodynamic work. Systems that contain gases at high pressures or concentrated solutions that deviate substantially from ideal behavior require the use of fugacities or activities, respectively.

Combining Equations 14.7.16 with  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  provides insight into how the components of  $\Delta G^\circ$  influence the magnitude of the equilibrium constant:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K \quad (14.7.17)$$

Notice that  $K$  becomes larger as  $\Delta S^\circ$  becomes more positive, indicating that the magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder. Moreover,  $K$  increases as  $\Delta H^\circ$  decreases. Thus the magnitude of the equilibrium constant is also directly influenced by the tendency of a system to seek the lowest energy state possible.

*The magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder and seek the lowest energy state possible.*

### Temperature Dependence of the Equilibrium Constant

The fact that  $\Delta G^\circ$  and  $K$  are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 14.7.17, which can be rearranged as follows:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (14.7.18)$$

Assuming  $\Delta H^\circ$  and  $\Delta S^\circ$  are temperature independent, for an exothermic reaction ( $\Delta H^\circ < 0$ ), the magnitude of  $K$  decreases with increasing temperature, whereas for an endothermic reaction ( $\Delta H^\circ > 0$ ), the magnitude of  $K$  increases with increasing temperature. The quantitative relationship expressed in Equation 14.7.18 agrees with the qualitative predictions made by applying Le Chatelier's principle. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of  $K$ . Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of  $K$ . Equation 14.7.18 also shows that the magnitude of  $\Delta H^\circ$  dictates how rapidly  $K$  changes as a function of temperature. In contrast, the magnitude and sign of  $\Delta S^\circ$  affect the magnitude of  $K$  but not its temperature dependence.

If we know the value of  $K$  at a given temperature and the value of  $\Delta H^\circ$  for a reaction, we can estimate the value of  $K$  at any other temperature, even in the absence of information on  $\Delta S^\circ$ . Suppose, for example, that  $K_1$  and  $K_2$  are the equilibrium constants for a reaction at temperatures  $T_1$  and  $T_2$ , respectively. Applying Equation 14.7.18 gives the following relationship at each temperature:

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \quad (14.7.19)$$

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} \quad (14.7.20)$$

Subtracting  $\ln K_1$  from  $\ln K_2$ ,

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (14.7.21)$$

Thus calculating  $\Delta H^\circ$  from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature ( $K_1$ ) allow us to calculate the value of the equilibrium constant at any other temperature ( $K_2$ ), assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of temperature. Equation 14.7.21 is often referred to as the **van 't Hoff equation** after Dutch chemist Jacobus Henricus van 't Hoff in 1884 in his book *Études de Dynamique chimique* (Studies in dynamic chemistry).

### ✓ Example 14.7.4

The equilibrium constant for the formation of  $\text{NH}_3$  from  $\text{H}_2$  and  $\text{N}_2$  at  $25^\circ\text{C}$  was calculated to be  $K_p = 5.4 \times 10^5$  in Example 14.7.2. What is  $K_p$  at  $500^\circ\text{C}$ ? (Use the data from Example 14.7.1)

**Given:** balanced chemical equation,  $\Delta H^\circ$ , initial and final  $T$ , and  $K_p$  at  $25^\circ\text{C}$

**Asked for:**  $K_p$  at  $500^\circ\text{C}$

**Strategy:**

Convert the initial and final temperatures to kelvin. Then substitute appropriate values into Equation 14.7.21 to obtain  $K_2$ , the equilibrium constant at the final temperature.

**Solution:**

The value of  $\Delta H^\circ$  for the reaction obtained using Hess's law is  $-91.8 \text{ kJ/mol}$  of  $\text{N}_2$ . If we set  $T_1 = 25^\circ\text{C} = 298 \text{ K}$  and  $T_2 = 500^\circ\text{C} = 773 \text{ K}$ , then from Equation 14.7.21 we obtain the following:

$$\begin{aligned}\ln \frac{K_2}{K_1} &= \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \\ &= \frac{(-91.8 \text{ kJ})(1000 \text{ J/kJ})}{8.314 \text{ J/K}} \left( \frac{1}{298 \text{ K}} - \frac{1}{773 \text{ K}} \right) = -22.8 \\ \frac{K_2}{K_1} &= 1.3 \times 10^{-10} \\ K_2 &= (5.4 \times 10^5)(1.3 \times 10^{-10}) = 7.0 \times 10^{-5}\end{aligned}$$

Thus at  $500^\circ\text{C}$ , the equilibrium strongly favors the reactants over the products.

### ? Exercise 14.7.4

The equilibrium constant for the reaction of  $\text{NO}$  with  $\text{O}_2$  to give  $\text{NO}_2$  at  $25^\circ\text{C}$  is  $K_p = 2.2 \times 10^{12}$ . Use the  $\Delta H_f^\circ$  values in the exercise in Example 14.7.4 to calculate  $K_p$  for this reaction at  $1000^\circ\text{C}$ .

**Answer**

$$5.6 \times 10^{-4}$$

## Summary

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express  $\Delta G$  in terms of the partial pressures of the reactants and products, which gives us a relationship between  $\Delta G$  and  $K_p$ , the equilibrium constant of a reaction involving gases, or  $K$ , the equilibrium constant expressed in terms of concentrations. If  $\Delta G^\circ < 0$ , then  $K$  or  $K_p > 1$ , and products are favored over reactants. If  $\Delta G^\circ > 0$ , then  $K$  or  $K_p < 1$ , and reactants are favored over products. If  $\Delta G^\circ = 0$ , then  $K$  or  $K_p = 1$ , and the system is at equilibrium. We can use the measured equilibrium constant  $K$  at one temperature and  $\Delta H^\circ$  to estimate the equilibrium constant for a reaction at any other temperature.

## Contributors and Attributions

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