

7.11 Gibbs Free Energy and Equilibrium

Skills to Develop

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

We have identified three criteria for whether a given reaction will occur spontaneously (that is, proceed in the forward direction, as written, to reach equilibrium): $\Delta S_{\text{univ}} > 0$, $\Delta G_{\text{sys}} < 0$, and the relative magnitude of the reaction quotient Q versus the equilibrium constant K . Recall that if $K > Q$, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if $K < Q$, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If $K = Q$, then the system is at equilibrium, and no net reaction occurs. Table 1 summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes.

Table 1: Criteria for the Spontaneity of a Process as Written

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

Because all three criteria are assessing 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 free energy change of reaction (ΔG) and the instantaneous reaction quotient (Q). To do so, we will first reveal the relationship between the standard free energy change of a reaction (ΔG°) and the equilibrium constant (K).

Free Energy and the Equilibrium Constant

Because ΔH° and ΔS° determine the magnitude of ΔG° 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 ΔG° and vice versa.

Combining terms gives the following relationship between ΔG and the reaction quotient Q :

$$\Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ + RT \ln K \quad (1)$$

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

$$0 = \Delta G^\circ + RT \ln K \quad (2)$$

$$\Delta G^\circ = -RT \ln K \quad (3)$$

If you combine equations 1 and 3, you get the equation

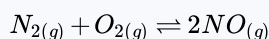
$$\Delta G = RT \ln \frac{Q}{K} \quad (4)$$

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

For a product-favored process under standard conditions, K is greater than 1.

Example 1

Calculate K for the reaction of O_2 with N_2 to give NO at 423 K:



ΔG° for this reaction is +22.7 kJ/mol of N_2 .

Given: ΔG° , and temperature

Asked for: K

Strategy:

Substitute values for ΔG° and T (in kelvin) into Equation 3 to calculate K, the equilibrium constant for the formation of nitrogen monoxide.

SOLUTION

For equilibrium conditions, rearranging Equation 3,

$$\Delta G^\circ = -RT \ln K_p \quad (5)$$

$$\frac{-\Delta G^\circ}{RT} = \ln K_p \quad (6)$$

Inserting the value of ΔG° and the temperature (423 K) into this equation,

$$\ln K = -\frac{(-22.7 \text{ kJ})(1000 \text{ J/kJ})}{(8.314 \text{ J/K})(423 \text{ K})} = -6.45 \quad (7)$$

$$K = 1.6 \times 10^{-3} \quad (8)$$

Thus the equilibrium constant for the formation of nitrogen monoxide at room temperature is less than 1. The reaction is reactant-favored at equilibrium.

Exercise 1

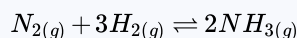
Calculate K for the reaction of NO with O_2 to give NO_2 at 25°C. ΔG° for this reaction is -70.5 kJ/mol of O_2 .

Answer

$$2.2 \times 10^{12}$$

Example 2

ΔG° is -32.7 kJ/mol of N_2 for the reaction at 100°C



Calculate ΔG for the same reaction under the following nonstandard conditions:

- $[N_2] = 2.00 \text{ M}$,
- $[H_2] = 7.00 \text{ M}$,
- $[NH_3] = 0.021 \text{ M}$,
- and T = 100°C.

In which direction must the reaction proceed to reach equilibrium?

Given: balanced chemical equation, molarity of each species, temperature, and ΔG°

Asked for: the direction in which the reaction will proceed to reach equilibrium

Strategy:

- Using the concentration values given, calculate Q.
- Using the value of ΔG° , calculate the value of K using Equation 3
- Substitute the values of K and Q into Equation 4 to obtain ΔG for the reaction under nonstandard conditions.

Solution:

A Using the equilibrium constant expression for the given reaction, we can calculate Q:

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

B Using the value of ΔG° , calculate the value of K

$$\Delta G^\circ = -32,700\text{J} = -(8.314 \frac{\text{J}}{\text{g}\cdot\text{K}})(373\text{K})\ln K \quad (9)$$

$$\frac{-32,700\text{J}}{-8.314 \frac{\text{J}}{\text{g}\cdot\text{K}} \cdot 373\text{K}} = \ln K \quad (10)$$

$$e^{10.54} = 38,000\text{J} = K \quad (11)$$

C Substituting the values of K and Q into Equation 1,

$$\begin{aligned} \Delta G &= RT \ln \frac{Q}{K} = (8.314\text{J/K})(373\text{K}) \left(\frac{1\text{kJ}}{1000\text{J}} \right) \ln \frac{6.4 \times 10^{-7}}{3.8 \times 10^4} \\ &= -77\text{ kJ}_2 \end{aligned}$$

Because $\Delta G < 0$ and $K > Q$, the reaction is spontaneous in the forward direction, as written. In other words, the reaction must proceed to the right to reach equilibrium.

Exercise 2

Calculate ΔG for the reaction $N_{2g} + O_{2(g)} \rightleftharpoons 2NO_g$ under the conditions: $T = 423\text{ K}$, $[NO] = 0.0100\text{ M}$, $[O_2] = 0.200\text{ M}$, and $[N_2] = 1.00 \times 10^{-4}\text{ M}$. The value of ΔG° for this reaction is $+22.7\text{ kJ}$. In which direction will the reaction proceed to reach equilibrium?

Answer

$\Delta G = +28.3\text{ kJ}$; the reaction is nonspontaneous to the right as written, so the reaction will go to the left to reach equilibrium. This can be verified by the fact that $K < Q$.

Temperature Dependence of the Equilibrium Constant

The fact that ΔG° and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 3, which can be rearranged as follows:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (12)$$

Assuming ΔH° and ΔS° 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 12 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 12 also shows that the magnitude of ΔH° dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of ΔS° 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 ΔH° for a reaction, we can estimate the value of K at any other temperature, even in the absence of information on ΔS° . 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 12 gives the following relationship at each temperature:

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \quad (13)$$

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} \quad (14)$$

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

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (15)$$

Thus calculating ΔH° 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 ΔH° and ΔS° are independent of temperature.

Summary

Both K and ΔG° can be used to predict the ratio of products to reactants at equilibrium for a given reaction. ΔG° is related to K by the equation $\Delta G^\circ = -RT \ln K$.

- If $\Delta G^\circ < 0$, then $K > 1$, and products are favored over reactants at equilibrium.
- If $\Delta G^\circ > 0$, then $K < 1$, and reactants are favored over products at equilibrium.
- If $\Delta G^\circ = 0$, then $K = 1$, and the amount of products will be roughly equal to the amount of reactants at equilibrium. This is a rare occurrence for chemical reactions.

If a system is not at equilibrium, ΔG and Q can be used to tell us in which direction the reaction must proceed to reach equilibrium.

ΔG is related to Q by the equation $\Delta G = RT \ln \frac{Q}{K}$.

- If $\Delta G < 0$, then $K > Q$, and the reaction must proceed to the right to reach equilibrium.
- If $\Delta G > 0$, then $K < Q$, and the reaction must proceed to the left to reach equilibrium.
- If $\Delta G = 0$, then $K = Q$, and the reaction is at equilibrium.

We can use the measured equilibrium constant K at one temperature, along with ΔH° to estimate the equilibrium constant for a reaction at any other temperature.

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